

The American Mineralogist

*Journal of the Mineralogical
Society of America*

Vol. 40

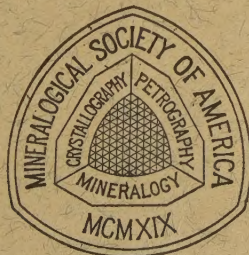
MARCH-APRIL, 1955

Nos 3 and 4

Contents

Screw dislocations and charge balance as factors of crystal growth.....	Sterling B. Hendricks	139
Synthesis and stability of minerals in the system $MgO-Al_2O_3-SiO_2-H_2O$	Della M. Roy and Rustum Roy	147
Simple method for the determination of the plagioclase feldspars.....	Wilfrid R. Foster	179
Directional grinding hardness in a diamond: A further study.....	Reynolds M. Denning	186
Trimorphism in zinc sulfide.....	Daniel C. Buck and Lester W. Strock	192
Rabbittite, a new uranyl carbonate from Utah.....	Mary E. Thompson, Alice D. Weeks and Alexander M. Sherwood	201
Navajoite, a new vanadium oxide from Arizona.....	Alice D. Weeks, Mary E. Thompson and Alexander M. Sherwood	207
Refinement of the structure of cubanite, $CuFe_2S_4$	Leonid V. Azaroff and M. J. Buerger	213
The crystal structure of berthierite, $FeSb_2S_4$	M. J. Buerger and Theodor Hahn	226
Stevensite, a montmorillonite-type mineral showing mixed-layer characteristics.....	G. W. Brindley	239
Crystallography of jadeite crystals from near Cloverdale, California.....	C. W. Wolfe	248
Application of the electron microscope to mineralogic studies.....	Edward Dwornik and Malcolm Ross	261
Baddeleyite from Phalaborwa, Eastern Transvaal.....	S. A. Hiemstra	275
Memorial of Lawson H. Bauer.....	Clifford Frondel	283
Memorial of Magnus Vonsen.....	George Switzer	286
Presentation of the Roebling Medal to Cecil Edgar Tilley.....	Arthur F. Buddington	289
Acceptance of the Roebling Medal.....	Cecil Edgar Tilley	292
Presentation of The Mineralogical Society of America Award to Hatten S. Yoder, Jr.....	J. F. Schairer	295
Acceptance of The Mineralogical Society of America Award.....	Hatten S. Yoder, Jr.	296

(continued on cover 2)



EDITOR: WALTER F. HUNT

ASSISTANT EDITOR: LEWIS S. RAMSDELL

BOARD OF ASSOCIATE EDITORS:

ELBURT F. OSBORN

IAN CAMPBELL

WILLIAM F. BRADLEY

ADOLF PABST (1955)

BRIAN MASON (1955-56)

FRANCIS J. TURNER (1955-57)

Proceedings of the thirty-fifth annual meeting of The Mineralogical Society of America at Los Angeles.....	C. S. Hurlbut, Jr.	299
Mineralogical Society (London).....		343
Notes and news: Oxidation of montmorillonite during laboratory grinding.....	W. D. Keller	348
Hydrohausmannite and hydrohetaerolite.....	A. D. Wadsley	349
Secondary alteration of chromite.....	E. den Tex	353
Note of the significance of "turbid" feldspars.....	Robert L. Folk	356
Spot grinding, a technique for finishing rock thin sections.....	Ronald Willden and David C. Arnold	357
Book reviews.....		360
New mineral names.....		367

Mineralogical Society of America

ASSOCIATED WITH THE GEOLOGICAL SOCIETY OF AMERICA

President: Harry H. Hess, Princeton University, Princeton, New Jersey.
Vice-President: Clifford Frondel, Harvard University, Cambridge 38, Massachusetts.
Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge 38, Massachusetts.
Treasurer: Earl Ingerson, U. S. Geological Survey, Washington 25, D. C.
Editor: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.
Councillors: Victor T. Allen, Institute of Geophysical Technology, St. Louis, Missouri.
C. Osborne Hutton, Stanford University, Palo Alto, California.
Felix Chayes, Geophysical Laboratory, Washington, D. C.
Leonard G. Berry, Queen's University, Kingston, Ontario, Canada.
Sterling B. Hendricks, U. S. Department of Agriculture, Beltsville, Maryland.

The enlarged issues of this journal for 1955 are made possible by a grant from the Penrose Fund of the Geological Society of America.

The American Mineralogist—Journal of the Mineralogical Society of America

A journal containing articles on mineralogy, crystallography, petrography, and allied sciences, is issued every two months. Contributions are invited from everyone. Office of Publication, Mineralogical Laboratory, Ann Arbor, Michigan.

The general conduct of the journal is in the hands of the editor, **Walter F. Hunt**, Ann Arbor, Michigan, to whom all manuscripts should be submitted. To assist the editor the council of the Mineralogical Society has appointed **Lewis S. Ramsdell**, Ann Arbor, Michigan, assistant editor, and the following board of associate editors:

William F. Bradley, Illinois State Geological Survey, Urbana, Illinois.
Ian Campbell, California Institute of Technology, Pasadena 4, California.
Brian H. Mason, American Museum of Natural History, New York, N. Y.
Elburt F. Osborn, Pennsylvania State College, State College, Pennsylvania.
Adolf Pabst, University of California, Berkeley 4, California.
Francis J. Turner, University of California, Berkeley 4, California.

It will expedite publication if two copies of each manuscript are submitted to the editor.

Sent to all members and fellows of the Mineralogical Society of America. Membership dues \$4.00 annually, fellowship dues \$5.00 annually. Subscriptions for libraries, colleges, institutions, companies and similar organizations \$6.00 annually.

Entered as second class matter at the post office at Menasha, Wis., under Act of March 3, 1879. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of Oct. 3, 1917, paragraph 4 section 429 P. L. & R. authorized March 13, 1922.

Notice of change of address, orders, and remittances should be sent to Dr. Earl Ingerson, U. S. Geological Survey, Washington 25, D. C.

Printed by the George Banta Publishing Company, Menasha, Wisconsin
Printed in the United States of America

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 40

MARCH-APRIL, 1955

Nos. 3 and 4

SCREW DISLOCATIONS AND CHARGE BALANCE AS FACTORS OF CRYSTAL GROWTH¹

STERLING B. HENDRICKS, *U. S. Department of Agriculture, Plant
Industry Station, Beltsville, Md.*

ABSTRACT

Screw dislocations in crystals are discussed and the growth spirals that arise from them are illustrated. A second general method of crystal growth is advanced. It depends upon the necessity of balancing the forces between ions or atoms at terminating crystal surfaces.

The importance of screw dislocations for crystal growth was stated by F. C. Frank at the symposium on "Crystal Growth" of the Faraday Society in 1948 (8, 9). This was soon followed by striking experimental verification (10, 1). Thus has opened a subject with many consequences in crystallography.

Frank's deduction was essentially of two parts. First, the observed rates of crystal growth at low supersaturation are too rapid to be explained by nucleation on flat surfaces (9). Second, growth can take place at the observed rate at the intersection of two surfaces in the reentrant angle of the surface step generated by emergence of the Burgers vectors. The background for this second deduction follows.

That the elastic strain of any rigid body can be resolved into six components with associated displacements was developed by V. Volterra in 1907 (13) and further formalized by A. E. H. Love in 1927 (11) who introduced the term "dislocation" in place of "distortioni" as used by Volterra. One of these six components of strain was shown by J. M. Burgers in 1939 (6) to be of the type shown in Fig. 1. In this figure the circuit, which is a path for integration, can be considered to be in the elastically deformed material surrounding an imperfection in a crystal (dislocation). Upon passing from *a* to *b* by a succession of primitive lattice translations, there is an error of closure represented by the vector \vec{s} . This vector, the Burgers vector or screw displacement, must be a vector sum

¹ Address, in part, of the retiring President of the Mineralogical Society of America, given at the thirty-fifth meeting of the Society in Los Angeles, California, November 2, 1954.

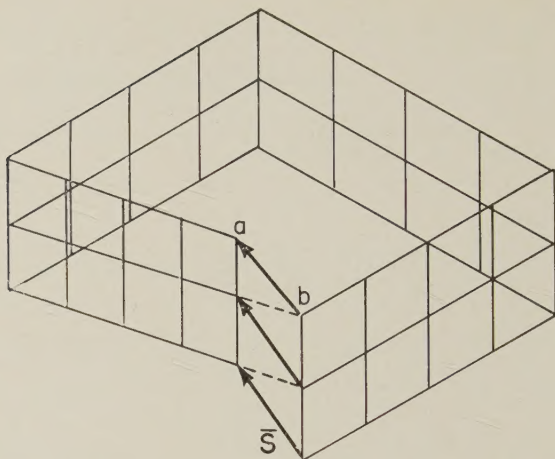


FIG. 1. The Burgers vector \bar{s} . The indicated circuit by primitive translations of the lattice is in elastically strained material around a dislocation.

of the elastically strained primitive translations of the lattice.

The Burgers vector \bar{s} is conserved along a cylinder which either must be closed upon itself, as a torus, for instance, or intersect the surface since, otherwise, the line integral of the elastic strain could not be conserved. Thus, a screw displacement of the lattice points on the surface can be generated. The entire volume of the crystal can develop by increments of growth about the screw axis without requiring fresh two dimensional nucleation. Conversely, the screw displacement is evident on a final crystal surface as a step, on a cleavage surface of mica, for instance, or as a spiral if lateral growth has taken place.

A screw displacement on a crystal surface is illustrated in Fig. 2. The surface is continuously warped such that as the growth front advances, clockwise in the illustration, by accretion of new material a helix of pitch \bar{s} is generated. In the center region the crystal is not defined; here the strain exceeds the elastic limit. This center region is the nucleus for crystallization as well as the region where etching starts. It has been observed to have a diameter as great as 35 microns (in biotite) and probably always exceeds many units of structure.

The growth spirals or helices are readily observed and have been described as found on many crystals (9, 2, 5). They generally can be seen at moderate magnification (say 200) and can be measured precisely by multiple beam interferometry. Several or many Burgers vectors might emerge on a crystal surface. In this case, they can interact to give figures in which the spiral character is not immediately evident (2). A simple

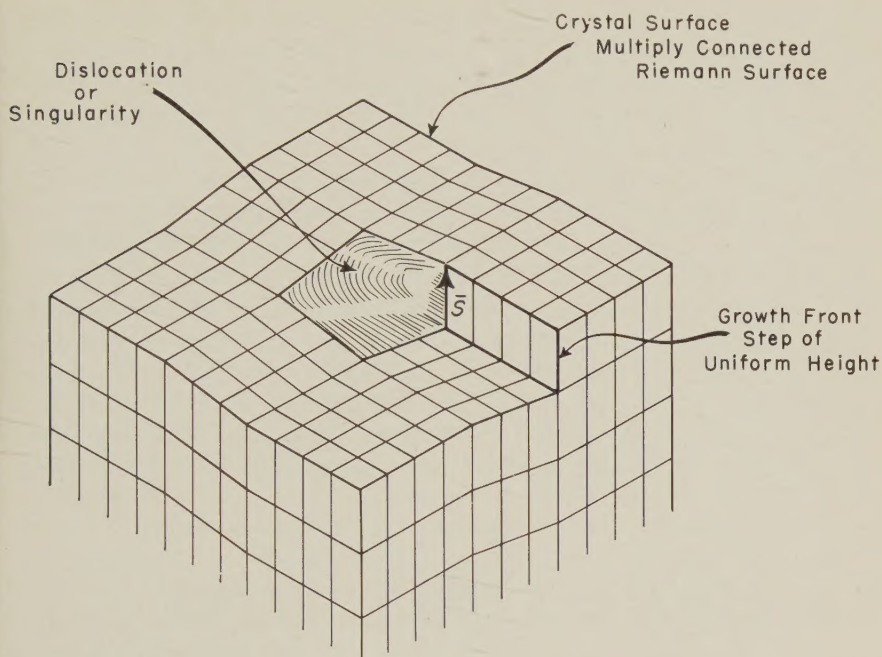


FIG. 2. A step on a crystal face arising from a screw dislocation which gives a growth front for extension of the crystal as a Riemann surface generated by the spiral.

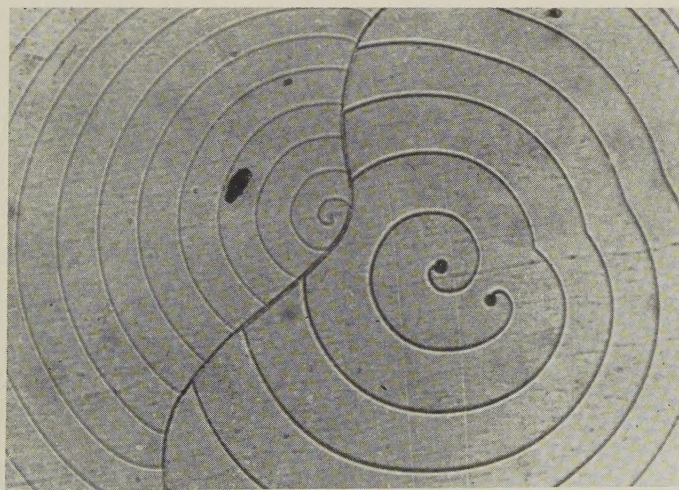


FIG. 3. Interaction of two spirals of equal \bar{s} but opposite rotation. A single spiral is shown on the right (SiC, courtesy W. Dekeyser and S. Amelinckx).

case is where two screw displacements are of equal pitch but opposite rotation as shown in Fig. 3. Then a succession of closed loops are present which spread outward as the crystal grows. An example of interaction between three growth spirals, taken from the work of S. Amelinckx (2), is reproduced as Fig. 4.

Growth on screw dislocations not only serves to account for observed rates of crystallization but also to preserve unusual sequences of layer succession in crystals having layer structures such as micas, SiC, graphite, etc. This was pointed out by S. Amelinckx and W. Dekeyser (5) for micas. In the polytypic polymorphism of these crystals there is a succession of layers, the individual arrangements of which can be represented by, say, *A*, *B*, and *C*. Thus, cubic close packing is *ABC ABC*—while hexagonal close packing is *ABABAB*—. Possibilities exist for other sequences such as *ABC ABAC ABC ABAC*—and some have been observed. Prior to the discovery of screw dislocations, presence of such



FIG. 4. Interaction of three growth spirals (schematic), two clockwise and one counterclockwise (after S. Amelinckx).

layer sequences seemed to imply interaction over long distances for repetition. But now it is evident that the repetition is preserved by the screw dislocation and that the repetition distance of the lattice is the pitch of the screw, or the displacement \bar{s} (5). In this way, too, might arise an orderly sequence of layers of different composition such as chlorite-mica-chlorite-mica—or vermiculite-mica-vermiculite-mica—of types which have been observed.

Growth of hopper shape crystals at liquid surfaces are also readily explained (4). In fact, observation of the growth spirals is very simple in such cases and those appearing on $K_4Fe(CN)_6$ or salol can be used for student demonstration experiments.

The very elegance of this advance and the extensive occurrence of screw dislocations in crystals, however, raise the danger that screw dislocations will be considered the only site of crystal growth at low supersaturations. Frank has avoided this implication, but Seitz (12), in an incidental discussion to a main purpose (essentially as an appreciation), states: "Frank has pointed out that dislocations catalyze crystal growth

so that an otherwise perfect crystal containing dislocations should grow far faster than one that does not. In fact, Frank's analysis shows that the presence of dislocations is almost a necessity for growth of crystals by vapor deposition or from solution in periods of time of every day or even geological interest." There is negative evidence, which truly might be only lack of observation, against the statement in the second sentence in that growth spirals have not been found on many crystals (calcite, sodium bromide) upon careful examination.

Actually, there is another general process for growth at low supersaturation and it is this process that is called "charge balance" in the title, a choice of term that might be none too happy. The process is really a result of Pauling's principle of microscopic neutrality (Electrostatic Valence Principle) which recognizes that in ionic crystals neutrality of surroundings is maintained among the immediate neighbors of an ion. Thus, a crystal containing silicate groups or any groups of atoms such as CO_3^{--} , SO_4^{--} , etc. brings up a more serious question of termination than of growth. Growth is by a leap-frog type process in which accretion of negative ions requires added positive ions which, in turn, requires further negative ions, etc. for charge balances. Nor is the process restricted to ionic substances, but might be expected in any case where the atomic arrangement is involved.

This process of growth was perhaps sensed by H. E. Buckley (7) who in discussing failure of concepts of theories of perfect lattices as controlling crystal growth developed by Kossel and Stranski, among others, points out: "Another difficulty arises because, so far, the problems in the calculations of crystal-surface force fields are so great that simplifying assumptions have to be made to render them capable of any solution at all. Such, for example, is that of assuming that ions to be spherically symmetrical (an assumption probably near the truth for rock salt ions). But to what extent can the consequences derived from these simplified cases be applied to more complex crystals with RO_4 ions, of perhaps not even regular tetrahedral shape?"

The lack of charge balance of an $(hk0)$ face of kaolinite is shown in plan and elevation in Fig. 5. The impossibility of both balancing the charge at the face and terminating the crystal without changing the structure from that of kaolinite can be appreciated. This difficulty can only be met by the presence of exchangeable ions and thus the surface differs in composition from the interior. But even the presence of these external ions would not prevent the charge pattern on $(hk0)$ from serving to continue growth.

The failure of charge balance at an $(hk0)$ surface of kaolinite essentially illustrates the situation for the structurally related micas. Growth spirals

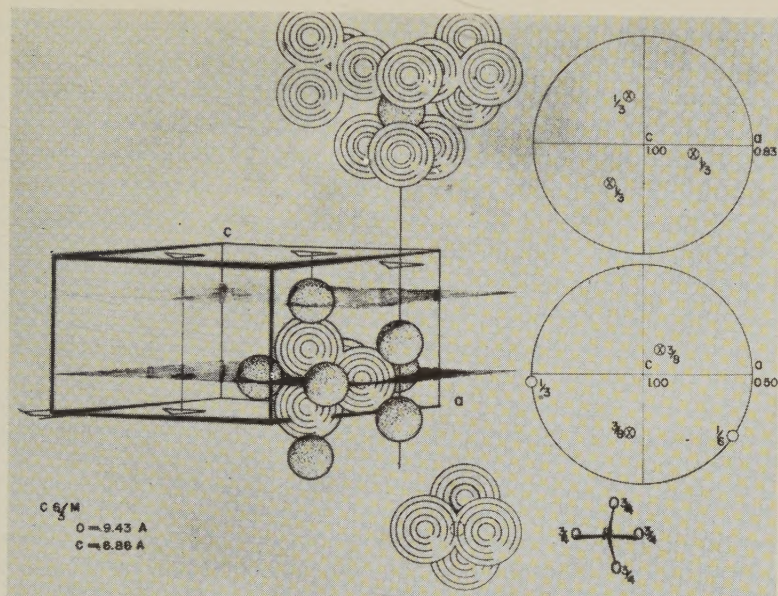


FIG. 6. Atomic arrangement on a $(10\bar{1}0)$ termination of apatite. The stereographic projections show the electrostatic valence distribution around Ca^{++} on a three-fold axis and oxygen of a PO_4^{---} group on the reflection plane.

can only be met by adding further PO_4^{---} ions. In a more formal way, this is shown by the stereographic projection for the components of electrostatic valence around a Ca^{++} ion on a three-fold axis and of an oxygen atom on a reflection plane. The growth then might be at the spiral front by the balancing of charge on this front.

Growth of alkali halide crystals are of interest in the bearing on both screw dislocations and balance of charge—or rather potential balance. Growth spirals have been observed on NaCl crystals and these crystals readily form in hopper shapes. If (100) is considered as a terminating surface, the charge distribution is balanced since at $(100)_0$ and $(100)_{1/2}$ Na^+ and Cl^- are equivalently surrounded and thus would not serve for continued growth. But as the size of the negative ion is increased, as in NaBr, this ion deviates from being essentially a point charge. In such crystals the detailed balancing at the surface could be important for continuing growth.

ACKNOWLEDGMENT

Frank's first publication on growth spirals in the Transactions of the Faraday Society in 1949 was a striking example of deduction, but I did not comprehend the wide implications until reports of observation on

many crystals shortly began to appear. Among these were numerous examples due to Prof. W. Dekeyser and Dr. S. Amelinckx of the Laboratorium Voor Kristalkunde, Geologisch Instituut, University of Ghent, Ghent, Belgium. I spent a short time in Ghent in September, 1954, discussing the phenomena and in making some of the simpler observations and measurements with the guidance of Dr. Amelinckx. Photographs from which Fig. 3 was selected were supplied by Prof. Dekeyser and Dr. Amelinckx. The effect of charge balance on crystal growth was also raised with Prof. Dekeyser and the example of sodium bromide was suggested by him. The concept seemed already to be part of his thinking and it might well have been stated some place in the older literature.

REFERENCES

1. AMELINCKX, S., *Nature*, **167**, 939 (1951); **168**, 431 (1951), *Jour. de Chim. Phys.*, **48**, 425 (1951).
2. AMELINCKX, S., *Jour. de Chim. Phys.*, **49**, 411 (1952).
3. AMELINCKX, S., *Nature*, **170**, 760 (1952).
4. AMELINCKX, S., *Jour. de Chim. Phys.*, **50**, 218 (1953).
5. AMELINCKX, S., AND DEKEYSER, W., *Cong. Geol. Int. Algiers*, 1952, **18**, 9 (1953).
6. BURGERS, J. M., *Proc. Acad. Sci., Amsterdam*, **42**, 293 (1939); **42**, 378 (1939).
7. BUCKLEY, H. E., *Crystal Growth*, John Wiley & Sons, New York (1951), p. 178.
8. FRANK, C. F., *Discussions of the Faraday Soc.*, **5**, 48 (1949).
9. FRANK, F. C., *Advances in Physics*, **1**, 91 (1952).
10. GRIFFIN, L. J., *Phil. Mag.*, **41**, 196 (1950).
11. LOVE, A. E. H., *The Mathematical Theory of Elasticity*, Cambridge Univ. Press (1927).
12. SEITZ, F., *Imperfections in Nearly Perfect Crystals*. John Wiley & Sons, New York (1952), p. 40.
13. VOLTERRA, V., *Ann. Ecole Norm. Super.*, **24**, 400 (1907).

SYNTHESIS AND STABILITY OF MINERALS IN THE SYSTEM $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}^*$

DELLA M. ROY AND RUSTUM ROY†

ABSTRACT

Phase equilibria in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ were studied in order to obtain further information on the stability of metamorphic minerals and mineral assemblages. The equilibria are described in terms of composition triangles, of phases in equilibrium with H_2O . Seventeen sets of triangles are given to describe changing equilibria with increasing temperature, at a constant water pressure of 10,000 psi. Syntheses of phases and equilibrium data are discussed, along with factors influencing the attainment of equilibrium.

At low temperatures montmorillonite "solid solutions" cover a large field in the high-silica portion of the diagram, whereas mixtures high in magnesia yield aluminian serpentine, in combination with other phases. Alumina hydrates and kaolinite dominate the high-alumina portion of the diagram in this temperature range. Aluminian serpentine at higher temperatures gives way to clinocllore. Cordierite, the only anhydrous ternary phase encountered, is stable in equilibrium with H_2O above ca. 500°C ., and the stable joins, quartz-cordierite- H_2O and cordierite-spinel- H_2O , divide the quaternary system into two areas: that part dominated by the aluminosilicates, and the area involving magnesium silicates. In the alumina-silica side of the system pyrophyllite is the hydrate stable to the highest temperature, 575°C .; but in the magnesia-silica side, talc is stable to a much higher temperature, 780°C . Applications of the data obtained to geologic problems are discussed.

INTRODUCTION

An understanding of the phase equilibria among common metamorphic minerals is of the utmost importance for a correct interpretation of the manner of formation of metamorphic rocks. The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ is of considerable interest, for it contains a large number of common metamorphic minerals, among them the anhydrous minerals, spinel, enstatite, forsterite, andalusite, kyanite, sillimanite, mullite; the alumina hydrates; clays of the kaolinite and montmorillonite groups; and chlorites and amphiboles. The determination of the phase equilibrium relations among the various minerals would provide information on formation of certain mineral assemblages, and furthermore provide a framework for the systematic addition of other components.

Moreover, the importance of this system is not limited to metamorphic rocks: it is also the basic system conditioning the relations among the minerals formed in argillaceous sediments. It is the only quaternary system involving not only typical but all the common clay minerals, and as such its study is basic to the whole field of clay and soil mineralogy.

* Contribution No. 53-60, Mineral Industries Experiment Station, College of Mineral Industries, The Pennsylvania State University, State College, Pennsylvania.

† Part of this work was submitted as a dissertation for the Ph.D. degree by D. M. Roy, The Pennsylvania State University, Division of Mineralogy, January 1952.

Besides these general considerations the solution of several specific problems in metamorphic and sedimentary petrology could be greatly furthered by the knowledge of phase equilibria in this system. Such problems involve for instance the determination of the conditions of stability of assemblages involving cordierite, one of the more common metamorphic minerals. Thus, the cordierite-forsterite-spinel combination (a stable triangle at solidus temperatures in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$) is incompatible with the association, cordierite-enstatite-spinel (a more common metamorphic assemblage). Other problems include the alternative between the stable associations of cordierite and corundum, or of mullite and spinel; both combinations occur in nature, but they represent a "crossed" relationship on the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ diagram.

A determination of the phase equilibria in the four-component system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ involves the equilibria in the four bounding ternary systems, which have been described in some detail. Envisioning the system as a tetrahedron with $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ as the base and H_2O at the apex, the other three sides are composed of the ternary systems, $\text{MgO-SiO}_2\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$. The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ was investigated by Rankin and Merwin (1918) and later modified by Bowen and Greig (1924), Greig (1927), and recently by Foster (1950) and Keith and Schairer (1952). The system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ was studied by Bowen and Tuttle (1949), the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ by Roy and Osborn (1952*a*, 1954) and the system $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$ by Roy, Roy and Osborn (1953). The present work in the quaternary system (see Roy, 1952) was carried out contemporaneously with that of Yoder (1952) in an attempt to add to the previous knowledge and obtain a more complete picture of the quaternary equilibria.

The importance of H_2O as a component for study of equilibria in metamorphic mineral systems has been ably demonstrated in the studies of the systems $\text{MgO-SiO}_2\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$ referred to above, and in other hydrothermal studies. The use of H_2O as one component enables one to study certain anhydrous mineral equilibria at subsolidus temperatures which may approach the temperature of formation of "high-rank" metamorphic rocks. In addition, at successively lower temperatures various hydrates are stable in the presence of excess H_2O , and the "lower-grade" metamorphic rock mineral families of amphiboles and chlorites are encountered. At still lower temperatures the layer lattice clay minerals are stable.

EXPERIMENTAL

Equipment

A hydrothermal assemblage employing several types of high-pressure vessels was used, enabling the attainment of water pressures up to a

maximum of 40,000 psi and temperatures up to 900° C. The following types of pressure vessel were used, some of which are standard equipment, and others developed in this laboratory: (1) Morey-type closed bomb (Morey and Ingerson, 1937) of 20 cc. capacity, top of 41 50 Cr-Mo steel and bottom of 18-8 stainless steel. The practical upper temperature limit was 550° C. at 10,000 psi, (2) 4 cc. capacity bomb of the above type, top and bottom both of 316 stainless steel. Temperatures of 600° C. at 10,000 psi were easily maintained. These have the further advantage of being cheaper, (3) Tuttle apparatus (Tuttle, 1949), using various sizes of small capacity stainless steel, Inconel-X and Stellite vessels. Temperatures up to 900° C. at 5,000 psi could be sustained, (4) "Test-tube" bomb (Roy and Osborn (1952*b*)) essentially a thick-walled steel test-tube attached to pressure tubing by a cone-in cone seal, about 8-9 inches long, $\frac{3}{4}$ -1 $\frac{1}{2}$ inches outer diameter and $\frac{1}{8}$ - $\frac{1}{4}$ " i.d., made of stainless steel, Inconel-X and Stellite. Temperatures up to 850° C. at 5,000 psi could be maintained indefinitely using the latter alloy. Shorter runs of several hours could be made up to 925° C.

Pressure was generated by three types of pumps: (1) A piston-type pump operating on water, supplied by American Instrument Company, (2) A pump manufactured by Sprague Instrument Company, based on the pressure multiplying piston working off laboratory air pressure and supplying a relatively large volume of fluid per stroke, was used up to 25,000 psi, (3) A "jack-type" pump (Roy and Osborn, 1952*b*) in which the pressure is generated by compression of water in a stainless steel chamber by a commercial "jack." This pump was most useful for attaining high pressures quickly.

The vessels were attached by pressure tubing through a system of valves and bourdon-type gauges to the pumps described above, so that each vessel could be independently maintained at a specific temperature and pressure. The vessels were heated in chromel-wound furnaces, the temperatures being automatically regulated.

An additional assemblage used was a grinding apparatus (Roy and Osborn, 1952*b*) consisting of closed Morey-type bombs containing the sample, a determined quantity of water, and several stainless steel rods. The bombs were attached to shafts and rotated by a chain drive, and heated in chromel-wound furnaces. The samples were thereby subjected to grinding action while they were heated under H_2O pressure. Satisfactory runs could be made up to only 450° C. at approximately 10,000 psi.

In general, the accuracy of the temperature control was of the order of $\pm 3^\circ$ C., but considering the differences among the different types of vessels an overall reproducibility of $\pm 5^\circ$ can be attained in the not unfavorable cases. Especially since the effect of pressure was slight in most cases, no effort was made to calibrate the pressure gauges, except to check

several gauges against one another. Pressures are therefore only accurate to about $\pm 3\%$ of the value given.

Starting Materials

Natural minerals, synthetic minerals, and various chemical mixtures, which in some cases required purification, were used as starting materials. Among the natural minerals used were the following: Cordierite from Möreland, Kragero, Norway, U. S. National Museum, No. R-6993; spinel (ruby) from Ceylon, Genth collection, No. 234.2, The Pennsylvania State University; sapphirine from Fiskernäs, Greenland, USNM No. 94335; andalusite from Custer, S. Dakota; kaolinite from Macon, Georgia, A.P.I. No. 3; Langley kaolinite, and Florida kaolinite; clinocllore from Westchester, Chester County, Pa., Genth collection, No. 468.4. Synthetic minerals were prepared as described in the section on synthesis.

In some cases mechanical mixtures of reactive C.P. oxides were used; e.g., MgO or MgCO_3 , $\gamma\text{-Al}_2\text{O}_3$, and silicic acid. In the glass-forming area glasses were prepared, but most frequently used was a mixture prepared from solution which could be made for any composition. Magnesium and aluminum nitrates were dissolved together in a minimum amount of water, ethyl orthosilicate was dissolved in alcohol, the two solutions mixed together in excess alcohol, evaporated gently until a rigid gel formed, and heated to about 400°C . to decompose the salts, leaving an intimate oxide "gel," possessing little if any long range order. The general applicability, the relative ease of making the mixtures combined with the rapidity of operation lead us to recommend the method for phase equilibrium studies in both "dry" and "wet" systems.

Techniques

The samples were prepared by one of the methods described above, then a small amount of sample put in a gold or platinum envelope, and in most cases surrounded by a larger envelope containing more of the sample as a buffer. One to four samples were heated in a bomb at the desired temperature and pressure for periods from a few hours to several weeks, the longer periods usually being required to approach a condition of equilibrium. In some cases the grinding apparatus was used, particularly to study the decomposition of a mineral which was not realized by ordinary hydrothermal treatment. After a run the bomb was quenched in a vessel or stream of water, in attempt to arrest the equilibrium, requiring usually less than 15 seconds to reach 100°C . and $\frac{1}{2}$ to 5 minutes to reach room temperature. It should be mentioned that in no case other than for the brucite-periclase transition was difficulty in arresting the equilibrium encountered using the technique described.

Identification

The phases present in the products were identified in all cases by their x-ray diffraction patterns, using either Norelco 90° instrument or a G.E. XRD-3 165° diffractometer, employing filtered Cu radiation. Usually the samples were also studied under the petrographic microscope, though in most instances the crystal size of the product was too small to enable positive identification optically. When necessary, observations were

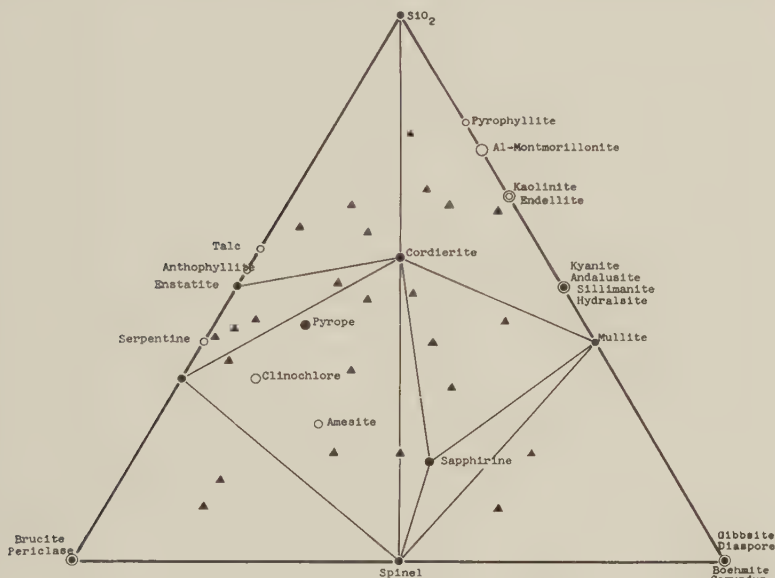


FIG. 1. Compositions studied in the system $MgO-Al_2O_3-SiO_2-H_2O$, projected on the $MgO-Al_2O_3-SiO_2$ base.

Open circles are used to indicate the compositions of hydrated minerals (which do not lie on the base of the tetrahedron) and solid circles, anhydrous mineral phases. Triangles show the compositions of other mixtures studied.

made under the electron microscope, RCA EMU model; and differential thermal analysis was employed for certain problems.

RESULTS

Synthesis of Minerals

Minerals encountered. The composition of minerals occurring in the system $MgO-Al_2O_3-SiO_2-H_2O$ is given in Fig. 1 as a projection on the $MgO-Al_2O_3-SiO_2$ base, along with other points representing compositions of mixtures used. In addition to the simple oxide components, the minerals synthesized in the present study were the following:

<i>Anhydrous</i>		<i>Hydrous</i>	
Mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Brucite	$\text{Mg}(\text{OH})_2$
Andalusite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Enstatite	$\text{MgO} \cdot \text{SiO}_2$	Boehmite, Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Forsterite	$2\text{MgO} \cdot \text{SiO}_2$	Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	Hydralsite	$2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$
Cordierite	$2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$	Pyrophyllite	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
		Talc	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
		Montmorillonite	variable, Mg-Al-Si
		Clinochlore	$5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
		Aluminian Serpentine	$5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$

Absences. Notable absences among the anhydrous minerals synthesized are sillimanite, kyanite, pyrope and sapphirine, and among the hydrous minerals the anthophyllite-gedrite amphiboles. All attempts to synthesize these minerals as equilibrium phases failed. The synthesis of sillimanite has been reported previously (Morey, 1942; Balconi, 1941; Michel-Levy, 1950), but because of similarities to mullite, it is doubtful if identification of the product of synthesis was positive. The synthesis of kyanite or pyrope has not been reported. Sapphirine was found to have a small stability field in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at liquidus and solidus temperatures (Foster, 1950, Keith and Schairer, 1952), but was not encountered in the present study as a stable phase at lower temperatures (below 900°C.) in the presence of excess water. It has been decomposed, however, by grinding at 390°C. and 5,000 psi.

Syntheses of Interest

Andalusite was synthesized in the present study, probably for the first time. Synthesis was achieved from alumina-silica mixtures only in the presence of seeds of natural andalusite. The addition of a small amount of MgO , however, apparently aided the crystallization, and andalusite was formed from such mixtures in the absence of seed crystals. Hydrothermal treatment of various kaolinite samples (Langley, Macon and Florida) also yielded the mineral, and it is suggested that the presence of impurities may play a role in its formation. No definite stability range was established, but andalusite formed in the temperature range $450\text{--}700^\circ\text{C.}$, with H_2O pressures of 10,000 to 30,000 psi, higher pressures definitely favoring its formation. It is conceivable that andalusite is metastable in this pressure range and that mullite is the only stable aluminosilicate below 30,000 psi. A more complete description of the synthesis is given by Roy (1954).

Hydralsite has been described by Roy and Osborn (1952a, 1954) in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, and is believed to be a micaceous type of crystal, related to pyrophyllite, but having a composition of approximately

$2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$. This phase was also formed as one product from mixtures in the system $MgO-Al_2O_3-SiO_2-H_2O$, at temperatures ranging from about 410 to 550° C., with H_2O pressures of 5,000 to 20,000 psi. Whether or not Mg^{2+} enters the structure has not been established. The apparent "stability" of this phase in the presence of Mg^{2+} , however, suggests that such a structure is the easiest one to form from mixtures relatively high in alumina, above the upper stability temperature of kaolinite, in the absence of large cations which would bring about the formation of a true mica.

Serpentine phases. The question of the control of morphology by composition was investigated by Roy and Roy (1952, 1954) by synthesizing a large number of serpentine-like phases containing ions of varying sizes in both the tetrahedral and octahedral layers. It was established that composition was a necessary but not sufficient consideration in determining the morphology of the mineral formed. Starting with chrysotile, $Mg_6Si_4O_{10}(OH)_8$, and attempting various substitutions, the most important among the substituent ions was Al^{3+} for Mg^{2+} and Si^{4+} . It is of considerable interest to note that the substitution was not of the heptaphyllitic-octophyllitic variety—that is, the introduction of Mg^{2+} ions into the vacant octahedral lattice positions of the octahedral layer in kaolinite, or the formation of vacant sites by substituting Al ions into the octahedral Mg layer of chrysotile. In other words, there is no solid solution between kaolinite and chrysotile.* The substitution takes place only by the very common mechanism of the exchange of $2Al^{3+}$ ions for $1Mg^{2+}$ and $1Si^{4+}$ ion. Along a composition line extending outwards from the chrysotile composition a single "aluminian serpentine" phase is obtained, up to and including the composition $5MgO:1Al_2O_3:3SiO_2$. This composition corresponds to the substitution of $2(Al^{3+})$ ions for $(Mg^{2+} + Si^{4+})$ in the chrysotile formula. Further data obtained on a mixture with higher Al_2O_3 content (see Table 1, mixture XL1, reaction 14) ($50:30:20$, $MgO:Al_2O_3:SiO_2$) indicate that, although from this composition at temperatures between 350° C. and 640° C. a serpentine phase is obtained along with other phases, the serpentine phase is not identical with that obtained from the $5MgO:1Al_2O_3:3SiO_2$ composition the basal spacings being somewhat smaller—7.07 Å rather than 7.17 Å. This would indicate that the limit of the substitution is not reached when $1Mg^{2+}$ and $1Si^{4+}$ ion have been replaced by $2Al^{3+}$ ions and may extend as far as amesite. The actual extent of solid solution and the relation to

* That such solid solution does not exist or at least is not extensive is further demonstrated by the fact that the montmorillonite field intersects the chrysotile-kaolinite join (see triangles 1-4, Fig. 3).

TABLE 1. PHASE EQUILIBRIUM DATA FOR THE SYSTEM $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

MgO	Compo- sition Mol. % Al_2O_3	SiO_2	Run No.	Temp. $^{\circ}\text{C}$.	Press. psi	Time days	Phases Present*
2. Magnesium Montmorillonite \rightleftharpoons Talc + H_2O							
43		57	5251	230	5,000	5	Monty?
43		57	5252	230	5,000	29	Monty?
43		57	5313	275	10,000	21	Talc
4. Brucite + Diaspore \rightleftharpoons Spinel + H_2O							
40	25	35	5321	350	10,000	5	AS + l boehm
			5238	495	20,000	24	AS + spinel
50	30	20	5380	350	20,000	7	Boehm + AS
26	42	32	5317	350	10,000	5	Boehm + AS?
	42		5241	495	20,000	24	AS + cor? + spinel?
5. Kaolinite \rightleftharpoons Hydralite + Al-M + H_2O							
12	44	44	5361	398	10,000	5	Kaol + l monty
	44		5359	410	20,000	6	Monty + hyd + AS
3	33	64	5324	372	10,000	4	Kaol + v l monty
			5360	398	10,000	5	Kaol + l hyd + monty
			5310	410	20,000	4	Monty + hyd + l AS
9. Montmorillonite \rightleftharpoons Pyroph. + Hyd + AS + H_2O							
35	4	61	F-308	390	20,000	5	Monty
35	4	61	5442	425	5,000	4	Talc + monty
25	10	65	5517	365	8,000	8.5	Monty
25	10	75	5170	420	20,000	18	Monty
25	10	65	5150	475	20,000	6	Crist + ?
25	10	65	5015	500	4,000	11	Talc + ?
9.5	12.5	78	4511	350	20,000	7	Monty
	12.5		F-309	390	20,000	5	Monty
	12.5		5303	450	20,000	4	Monty + l crist
	12.5		5148	470	20,000	6	Pyroph + crist
3	33	64	5379	350	20,000	7	Kaol + l monty
	33		5310	410	20,000	4	Monty + hyd + l kaol
10	25	65	5190	350	20,000	9	Monty
	25		5269	435	20,000	5	Monty (+ v l hyd?)
	25		5206	450	20,000	15	Monty + hyd + pyroph
50	6	44	4793	450	5,000	7	Mont + AS
50	6	44	4816	450	10,000	11.5	Mont + AS
54	3	43	4809	410	5,000	5.5	AS
10	25	65	5149	470	20,000	16	Monty + pyroph + hyd?
			5209	490	20,000	13	Hyd + AS
12	44	44	5361	398	10,000	5	Kaol + l monty
	44		5359	410	20,000	6	Hyd + AS + monty
	44		5291	475	20,000	6	Hyd + l AS + v l monty
	44		5208	490	20,000	13	Hyd + AS? + and
22	22	56	4490	360	12,000	10	Monty + AS?
	22		5310	410	10,000	4	Monty

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al_2O_3	SiO_2	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*
	22		5305	410	20,000	4	Monty+1 AS
	22		5258	450	20,000	27	AS+clinochlore(+?)
	22		5152	475	20,000	6	AS+pyroph+monty?
	22		4980	520	7,500	13	Cord+talc?
	10. Pyroph+AS (or Cl)+Hyd (or and.) \rightleftharpoons Cordierite+H ₂ O						
22	22	56	5256	455	20,000	16	Pyroph+AS+?
	22		5152	475	20,000	6	AS+pyroph+Cl?
	22		4716	500	5,000	7	Cl+AS
	22		4980	520	7,500	13	Cord (+pyroph?)
	22		4939	530	8,000	10	Cord+pyroph
	22		4664	545	16,000	30	Cord+Cl+mull
22	22	56 ⁿ	4628	300	15,000	25	Cord+AS+Cl
	22	56 ^{ng}	4720	400	3,000	3	Cord+1 AS?
	22	56 ^{ng}	4903	400	5,000	13	Cord+AS
	22	56 ^{ng}	5099	465	5,000	8	Cord+1 AS
	22	56 ^{ng}	5110	475	5,000	20	Cord+v 1 AS
31	20.9	48.1	5121	515	10,000	22	Cord+AS+crist+mull?
	20.9		5118	600	20,000	20	Cl (+AS)+cord+1 spinel (+cor?)
40	25	35	4990	565	5,000	13	Cord+AS+spinel
	25		5236	595	10,000	24	Cord+AS (+1 Cl)+spi- nel (+1 cor?)
50	30	20	4989	565	5,000	13	AS+spinel+cord?
23	28	49	5122	515	10,000	22	Crist+cord+AS+mull?
26	42	32	4984	645	5,000	15	Spinel+mull+cord+cor
	42		4987	565	5,000	13	Cord+spinel
	42		5145	695	20,000	8	Cord+cor+spinel
4	5	2	4267	450	7,500	11	AS+cor+spinel
4	5	2	5002	580	4,000	14	Cord+spinel+mull
4	5	2	4239	675	8,000	14	Cord+cor+spinel
12	44	44	5213	530	20,000	18	And+1 cord+1 cor+1 AS
	44		5339	575	30,000	5	Cord+cor
	44		5180	715	20,000	11	Cord+cor+mull
25	15	60	4979	520	7,500	13	Qtz+cord+talc
25	10	65	5150	475	20,000	6	Crist+AS?
	10		4868	500	12,000	7	Cl+AS
	10		5155	535	20,000	8	Cl+cord
10	25	65	5240	495	20,000	24	Hyd+AS+pyroph?
	25		4978	520	7,500	13	Qtz+mull+pyroph+cord
	25		5187	525	20,000	7	Hyd+?
	25		5228	525	30,000	4	Hyd+AS
	25		5212	530	20,000	18	Cord+crist
	25		5156	535	20,000	8	Pyroph+Cl+cord
	25		5384	535	20,000	10	Cord+hyd+AS+and +mull?
	25		4949	618	8,000	19	Cord+mull+crist

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al ₂ O ₃	SiO ₂	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*
12	20	68	4977	520	7,500	13	Qtz+cord+pyroph
9.5	12.5	78	5290	500	20,000	6	Pyroph+crist+l AS
	12.5		5154	535	20,000	8	Pyroph+crist+l AS cord+l
11. Aluminian serpentine (or Cl?) + brucite \rightleftharpoons forsterite + spinel + H ₂ O							
70	15	15	5273	500	10,000	3	AS+bru+spinel
	15		4898	510	10,000	14	Bru+AS+spinel
	15		5307	525	20,000	2	AS+bru+spinel
	15		5426	540	20,000	6	Bru+spinel+forst+AS
	15		4950	560	5,000	23	Spinel+forst+bru
	15		5418	560	20,000	1	Bru+spinel+forst+AS
75	15	10	5023	500	10,000	1	Bru+AS+spinel
	15		5314	500	20,000	2	AS+bru+spinel
	15		5367	500	25,000	11	AS+bru+spinel
	15		5027	510	10,000	0.5	Bru+AS+spinel
	15		4897	510	10,000	14	Bru+AS+spinel
	15		4974	520	7,500	13	Bru+forst+spinel
	15		5308	525	20,000	2	Bru+AS+spinel
	15		5226	525	30,000	4	Bru+AS+spinel
	15		5205	530	20,000	2	Bru+spinel+forst
	15		5233	535	30,000	3	Bru+spinel+forst
12. Pyroph \rightleftharpoons Mull (or and) + Qtz (Crist) + H ₂ O							
10	25	65	5156	536	20,000	8	Pyroph+Cl+cord
	25		5384	535	20,000	10	Cord+pyroph (?) + AS (?) +and (?) + l mull
	25		5175	555	15,000	10	Cord+crist+pyroph+ mull
	25		4953	560	5,000	23	Mull+cord+?
	25		5279	595	30,000	6	Cord+mull+cor?
	25		4949	618	8,000	19	Cord+mull+crist
9.5	12.5	78	5154	535	20,000	8	Pyroph+crist+l AS cord+l
	12.5		5174	555	15,000	10	Cord+pyroph+mull
	12.5		4953	560	5,000	23	Mull+crist+cord?
	12.5		5281	595	30,000	6	Cord+l Cl+l and+l mull
12a. Brucite \rightleftharpoons periclase + H ₂ O							
75	15	10	4880	625	12,000	1	Forst+spinel+bru
	15		4983	645	5,000	15	Forst+per+spinel
	15		4875	725	12,000	2	Forst+spinel+per
70	15	15	4881	625	12,000	1	Forst+spinel+l bru
	15		4605	705	10,000	8	Forst+spinel
14. Clinocllore \rightleftharpoons cord + forst + spinel + H ₂ O; and Clinocllore \rightleftharpoons AS							
56	11	33 ^{ng}	5492	300	5,000	120	Cl
56	11	33 ^{ng}	5298	400	5,000	25	Cl
56	11	33	5257	450	20,000	27	Cl+AS
	11		5294	475	20,000	6	Cl(?) + AS + l talc
56	11	33	5288	500	20,000	6	Cl (?) + AS
	11		5238	495	20,000	24	Cl+AS

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al_2O_3	SiO_2	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*
	11		5132	515	23,000	16	AS
	11		5133	515	23,000	16	AS
	11		4975	520	7,500	13	AS
	11		5234	535	30,000	3	AS
	11		5153	535	20,000	8	Cl+AS
	11		5173	555	15,000	10	AS+Cl+talc?
	11		5139	559	23,000	9	Cl+AS
	11		5138	559	23,000	9	AS
	11		4988	565	5,000	13	AS
	11		5071	605	10,000	7	AS+l talc+l spinel
	11		5235	595	10,000	24	AS+l Cl+talc+spinel
	11		5246	600	10,000	28	AS+l Cl+talc
	11		5117	600	20,000	20	Cl+AS+spinel
	11		5147	695	20,000	8	Cl+l talc
	11		5214	700	20,000	6	Cl+l spinel?
	11		5177	715	20,000	11	Forst+cord (+talc) +spinel
	11		4958	725	6,000	22	Forst+enst+spinel
	11		5158	735	20,000	2	Talc+forst+spinel
	11		5141	720	10,000	8	Cord+forst (+talc) +spinel
31	20.9	48.1	5121	515	10,000	22	Cord+AS+crist+mull?
	11		5136	605	10,000	16	Cord+AS+talc
	11		5118	600	20,000	20	Cl+cord+l spinel+AS +cor?
	11		5215	700	20,000	6	Cord+Cl
	11		5218	715	20,000	10	Cord+forst+l spinel
	11		5142	720	10,000	8	Cord+spinel+talc?
40	25	35	5022	670	10,000	7	Cord+talc+spinel
	25		5146	695	20,000	8	Cord+Cl+spinel
	25		4607	705	10,000	8	Talc+cord+spinel
	25		5157	738	20,000	2	Talc+cord+spinel
	25		5194	732	20,000	5	Cord+spinel+forst
	25		5007	745	10,000	10	Enst+spinel+cord
22	22	56	5258	450	20,000	27	AS+clinochlore (+?)
	22		5256	455	20,000	16	Pyroph+AS
15. $Talc \rightleftharpoons Enst + qtz + H_2O$							
25	10	65	5039	750	10,000	2½	Cord+talc+crist+qtz
	10		5183	775	15,000	5	Talc+cord (+crist?)
	10		4448	802	8,000	6	Cord+enst+crist
	10		5167	800	15,000	2	Cord+crist+enst
50	30	20	5166	800	15,000	2	Cord+spinel+forst
	30		4449	802	8,000	6	Spinel+enst
40	25	35	5165	800	15,000	2	Cord+spinel+enst
	25		4445	802	8,000	6	Cord+spinel+enst

n=natural mineral.

g=grinding run.

* Abbreviations used: Monty=montmorillonite; AS=aluminian serpentine; boehm=boehmite; cor=corundum; kaol=kaolinite; hyd=hydralsite; crist=cristobalite; pyroph=pyrophyllite; and=andalusite; cl=clinochlore; cord=cordierite; mull=mullite; qtz=quartz; bru=brucite; forst=forsterite; per=periclae; enst=enstatite; l=little. Al-M=aluminum montmorillonite.

the amesite problem is a subject for further detailed investigation.*

Aluminian serpentine is obtained from the lowest temperatures investigated (350°C.) up to a maximum of 650°C. at 10,000 psi in runs as long as 3 weeks. This phase yields a sharp x-ray pattern in contrast to the broadened reflections in the pattern for chrysotile; electron micrographs show the reason for this since, instead of the disordered tubes of chrysotile, well-formed hexagons are obtained with this composition (see Roy and Roy, 1954). However, this composition is also that of the chlorite clinochlore, and as Yoder (1952) first showed, on prolonged heating, under certain conditions the aluminian serpentine† converts to clinochlore. Yoder obtained partial or complete conversion of the aluminian serpentine to clinochlore in some runs (at 600°C. and 15,000 psi from its own composition). While using a pressure of 10,000 psi we found it virtually impossible to convert the serpentine to a chlorite. In later runs we demonstrated that both starting material and the pressure greatly affect the rate of this reaction. Using the organic-nitrate mixtures conversion is quite rapid (thus at 535°C. , 20,000 psi in 8 days most of the product is clinochlore). While no conversion has been possible below 10,000 psi and at this pressure runs as long as 24 and 28 days show only a very small amount of clinochlore, at a pressure of 23,000 psi a fair degree of conversion is achieved at the same temperature in 9 days (see data, Table 1, reaction 14). Thus whereas this does not demonstrate the existence of a "pressure bottom" for the formation of clinochlore—it does show that high pressures very greatly enhance the formation of this mineral.

The problem of the metastability of the aluminian serpentine is consequently not easily soluble; from our data it appears that clinochlore is the stable phase at least as low as 450°C. , at which temperature it forms slowly at the expense of the serpentine. The fact that it does not form below this temperature and also that we were not able to decompose it by "grinding" (see Roy and Osborn, 1952b) at 400°C. and 5,000 psi for 3 months, still do not prove that it (clinochlore) is not stable below this temperature. However, from the fact that chrysotile is stable up to 500°C. (at 15,000 psi) one would infer that the aluminian phase (of the 5:1:3 composition, or perhaps one containing a smaller percentage of Al_2O_3) has a true stability range, and persists metastably to much higher temperatures.

* Since this work was completed, extended study has been made of the magnesia-alumina chlorites by Nelson and Roy (1953).

† While this phase is here referred to as aluminian serpentine, it may very well correspond to "antigorite" in nature—indicating therefore that the essential difference between platy antigorite and tubular fibrous chrysotile is compositional, the additional R_2O_3 giving rise to the former.

The structural relationship between the aluminian serpentine and clinochlore also constitutes a very interesting problem. The former is a 2-layer structure, and the latter a 3-1-layer structure, illustrated in Fig. 2. One can immediately see that this constitutes a special type of polymorphism. The sequence of layers is identical: brucite-silica-brucite-silica in both cases. What is involved in the transition of aluminian serpentine to clinochlore is the rearrangement of bonds, so that every alternate layer of Si^{4+} ions in the silica layer has to completely sever its bonds

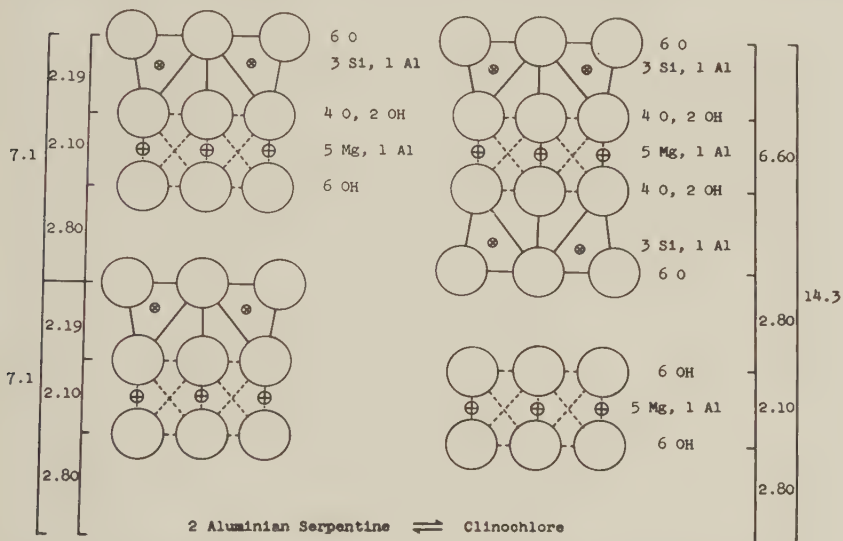


Fig. 2. Schematic diagram showing structural relationship between aluminian serpentine and clinochlore (a - b projection). Distances along the " c " axis are shown in Å.

with the O^{2-} ions of the original layer and form new Si-O bonds with the linked tetrahedra "pointing" in the opposite direction. The energy barrier to this major rearrangement must, of course, be very large and probably accounts for the extreme sluggishness of the reaction.

Montmorillonite. The synthesis of montmorillonite was achieved from a variety of compositions high in silica, and montmorillonites grown in different parts of the field were difficult to distinguish from one another because of the very small differences in lattice dimensions, or in expansion of the lattices upon introduction of a complex such as ethylene glycol. A number of compositions throughout a wide composition field produced essentially pure montmorillonite, e.g., the following molar ratios of $MgO-Al_2O_3-SiO_2$: 25:10:65; 22:22:56; 10:25:65 and 9.5:12.5:78.

In the system $Al_2O_3-SiO_2-H_2O$ (Roy and Osborn, 1952*a*, 1954) the

existence of a pure "aluminum montmorillonite" end-member was described, i.e., one with an ideal composition of about $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The possible existence of a pure magnesium montmorillonite, with a magnesia-silica ratio near that of talc, i.e., $3\text{MgO} : 4\text{SiO}_2$, was investigated. Talc was found to be stable as low as 275°C ., but at lower temperatures the x-ray pattern of the substance was much more diffuse, resembling a montmorillonite. Expansion of this lattice with ethylene glycol was attempted and the basal spacings were definitely affected but the pattern obtained was so weak that satisfactory measurable results could not be obtained (for further details see General Discussion). The substitution of as little as 4 mol. per cent Al_2O_3 in the talc composition yielded essentially a single phase montmorillonite, at temperatures up to 400°C . Approaching from the opposite side of the diagram, a large compositional area appeared to yield montmorillonite phases only.

It was hoped that information could be obtained as to whether there are two distant types of montmorillonite—i.e., the "heptaphyllitic" or beidellite type of montmorillonite, in which the octahedral layer consists largely of trivalent ions, and the "octaphyllitic" or saponite-hectorite type of montmorillonite in which the corresponding layer contains mostly bivalent ions. As discussed in a later section, it was substantiated that there is little, if any, solid solution between the higher temperature counterparts, talc and pyrophyllite, but a greater chance for extensive solid solution would be expected in the "looser" lower-temperature montmorillonite structures. The results in this aspect of the study were not positive, inasmuch as difficulty was encountered in distinguishing a high-magnesian montmorillonite from a high-aluminian montmorillonite by its x-ray diffraction pattern. A difference of about $.2\text{ \AA}$ was found in the basal spacings between the montmorillonites with less than 10 per cent Al_2O_3 and those having less than 10 per cent MgO ; the spacings for the former being 14.15 \AA and the latter 14.40 \AA (when treated and dried under identical conditions). Furthermore, using expansion with ethylene glycol, and attempting to obtain maximum resolution with $\frac{1}{5}^\circ$ per min. scanning the differences in spacing were approximately constant, 17.05 and 17.25 \AA for high magnesia and high alumina phases, respectively. While the second decimal place in the above figures is not significant the differences were real and reproducible at different times with different slides and instrument settings. The problem of the existence of solid solution among these end member types hinges on the ability to distinguish between the case where a single montmorillonite phase is present and the case in which two distinct montmorillonite phases co-exist. Therefore a mechanical mixture of a high magnesia and a high alumina phase was prepared and patterns were obtained after drying at 100°C . and also after saturation with ethylene glycol. It became evident

that the x-ray data would be far from unequivocal in their application to the problem at hand. Due to the width of the peaks (rarely less than $0.5^\circ 2\theta$ at half height for the single phases) the overlap was so great that in most cases the peak appeared to be single and only in the best cases after glycol saturation was even a suggestion of resolution observed. Attempts were also made to use the "b" spacing from the 060 line as a criterion for distinguishing between dioctahedral and trioctahedral types. While the typical "end members" could be easily distinguished, considerable ambiguity was again found in intermediate compositions. Only very extensive work on the product of each run may be able, therefore, to demonstrate the definite co-existence of 2 separate montmorillonite phases.* The present study appears to be fairly conclusive only insofar as it shows the existence of relatively pure "single" phase montmorillonites extending about 10 molar per cent into the diagram from each of the ternary systems. In the central area of the diagram we have assumed—in the absence of any definite contradictory evidence—that this solid solution is continued and thus gives rise to a complete series. Such an assumption also greatly simplifies the representation of the phase relations. As mentioned before, no accurate measurements of a pure magnesia-silica montmorillonite were obtained. However, a sharp discontinuity in expansion properties of montmorillonite was shown to exist on the Al_2O_3 side. A "pure" alumina-silica montmorillonite was found to expand with ethylene glycol only to 13.4 \AA .

From the data in Table 1 (reactions 2 and 9) it is seen that montmorillonite of apparently variable composition covers a large field at temperatures of about 350°C . or lower, but at higher temperatures the composition range becomes more limited. In the system $Al_2O_3-SiO_2-H_2O$ (Roy and Osborn, 1952*a*, 1954) the upper stability temperature of aluminum montmorillonite was set at about 420°C . The substitution of Mg into this lattice apparently increases the upper stability temperature of montmorillonite to about 480°C . A considerably extended investigation would be required to determine the composition of montmorillonite having the maximum stability temperature, but from the data obtained, its anhydrous composition must lie within the area bounded by the following compositions: 9.5:12.5:78, 25:10:65, and 10:25:65, $MgO:Al_2O_3:SiO_2$. A ratio of 15:15:70, in the center of this area, may therefore be suggested as the composition of the "ideally" stable montmorillonite.

Equilibrium Data

General statement. The results of more than 1,000 runs are summarized in Table 1. It would be extremely lengthy to include all the data, so

* This work is now in progress with a variety of synthetic montmorillonites.

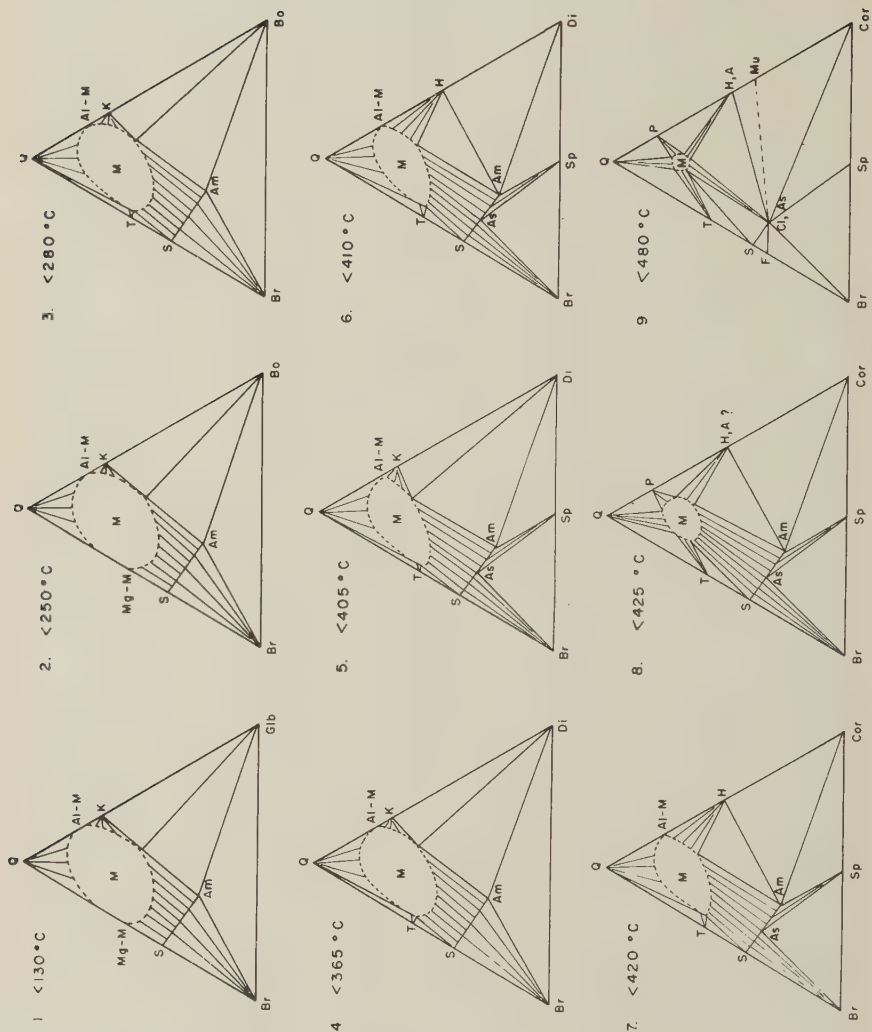
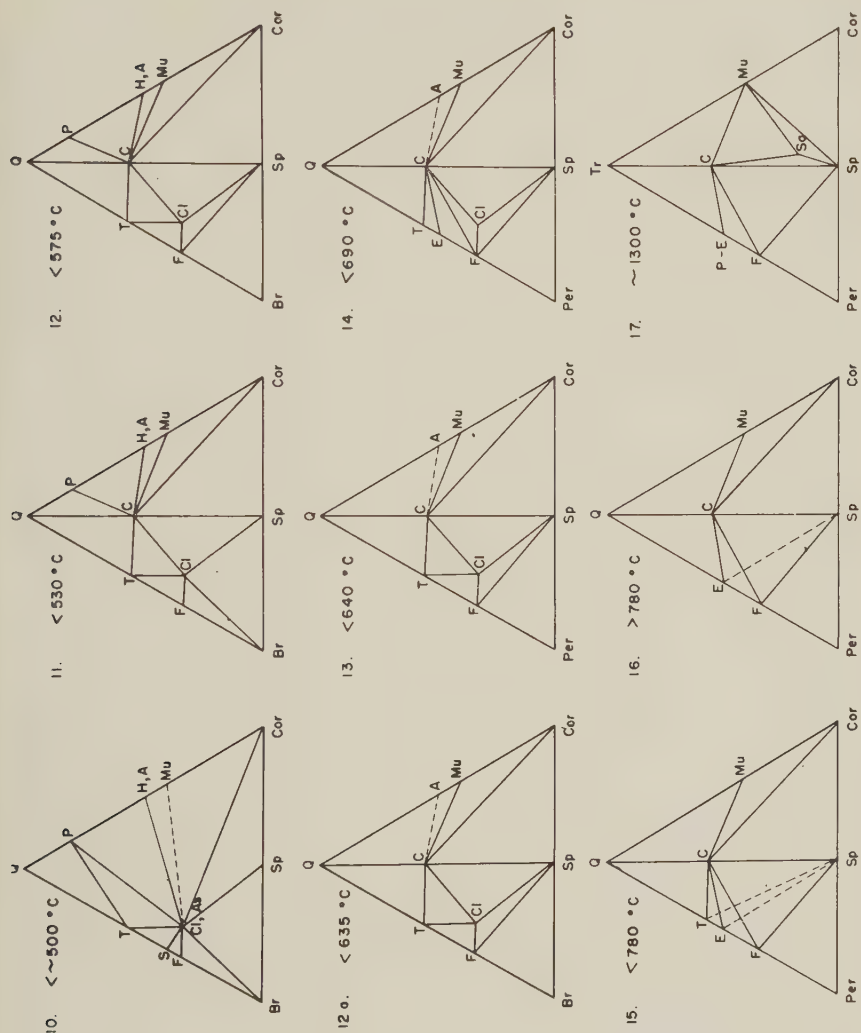


FIG. 3. The system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ showing compatibility triangles at a water pressure of 10,000 psi.

Abbreviations used: Br=brucite; Gib=gibbsite; S=serpentine; Mg-M=magnesium montmorillonite; M=montmorillonite; K=kaolinite; Al-M=aluminum montmorillonite; Q=quartz; Bo=boehmite; Am=amesite; T=talc; Di=diaspore; As=aluminian serpentine; Sp=spinel; H=hydralsite; A=andalusite; P=pyrophyllite; F=forsterite; Cl=clino-



chlore; Mu=mullite; Cor=corundum; C=cordierite; E=enstatite; Per=periclase; P-E=protoenstatite; Tr=tridymite; Sa=sapphirine. Triangle 17 represents "dry" equilibria at atmospheric pressure (See Foster, 1950).

Although it was recognized that there was appreciable solid solution in the 14 Å chlorite phase, due to lack of many data and for simplicity triangles 9-14 show the composition of this phase as a single point of the clinochlore composition.

only part of the runs were selected in order to describe a particular transition. The equilibria determined by these data are described by the compatibility triangles of Fig. 3, which represent tetrahedra in the four-component system with water at the apex of the tetrahedron; i.e., the triangles indicate combinations of three phases in equilibrium with water. At relatively low temperatures where hydrates are stable, other combinations of phases will exist when there is insufficient water to convert the assemblage entirely to hydrates. We therefore speak of two types of equilibria: those in the presence of excess water, and "water-deficient" triangles; the results of the present study concern only the former. A somewhat detailed discussion of the water-deficient region and a general treatment of the limitations to the application of such phase equilibrium data has been given by Roy (1953).

The equilibria described are an interpretation of our knowledge of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, using data reported by previous workers, as well as those obtained in the present study. In some cases it will be noted that only an approach to equilibrium has been attained, i.e., in addition to the equilibrium phases others may be present. The criterion used for determining equilibrium phases in such instances is that if increasing the period of time, keeping all other factors constant, increases the proportion of a given phase, then this is the more stable phase.

Factors influencing the attainment of equilibrium. The state of the starting material was found to play an important part in the attainment of equilibrium. Resistant minerals such as corundum might never be decomposed under the most extreme hydrothermal treatment, even with the use of grinding techniques. Other materials may react slowly but eventually attain equilibrium. Glasses are ordinarily desirable as hydrothermal starting materials; however, throughout much of the present system glasses could not be formed. Mechanical mixtures of C.P. chemicals in some cases yielded true equilibrium assemblages, but in many cases it was found that long periods of time were required to approach an equilibrium attained more quickly using either glasses, or mixtures prepared by the nitrate-ethyl silicate method

An example of the comparison of the mixed oxides and the nitrate-ethyl silicate decomposition product is seen in Table 1, reaction 14, runs numbers 5138 and 5139 under the composition 5:1:3 $\text{MgO:Al}_2\text{O}_3\text{:SiO}_2$. Clinocllore is presumably the stable phase under these conditions, but with similar duration of run very little clinocllore was crystallized from the oxide mixture, whereas the other yielded a considerable amount. Further data showing the effect of starting material are given in Table 2, which describe runs under similar conditions for 5 different types of mixture. The stable phase under the conditions of the runs is cordierite;

TABLE 2. EFFECT OF STARTING MATERIALS ON A TYPICAL COMPOSITION
Cordierite Composition

Mixture	Run No.	Temp. °C.	Press psi	Time days	Phases Present*
Oxide Mixture	4012	675	10,000	4	Crist+talc+cor
Gel+ $MgCO_3$	4014	675	10,000	4	Talc+mull
Gel+ $Mg(OH)_2$ gel	4125	735	5,000	5	Cord+talc+mull
Nitrate-ethyl silicate	4269	700	8,000	5	Cord+l cor +l spinel
Glass	4202	700	5,000	7	Cord+l talc +l mullite

* Abbreviations used: Crist=cristobalite; cor=corundum; mull=mullite; cord=cordierite; l=little.

however, the first two mixtures (mixed oxides, and coprecipitated alumina-silica gel+ $MgCO_3$) failed to yield cordierite at all. The third, (alumina-silica gel+ $Mg(OH)_2$ gel) yielded some cordierite with a large proportion of other phases, whereas the last two (nitrate-ethyl silicate and glass) yielded mostly cordierite with only small quantities of other phases.

The effect of high pressures was found in many cases to increase the rate of reaction. From the data obtained it was suggested that a pressure boundary may exist for certain reactions: for example, the transformation of aluminian serpentine to clinochlore, or of the pair, mullite-spinel to cordierite-corundum. Clinochlore was produced relatively easily at high temperatures under pressures of 20,000 psi or greater, but at 10,000 psi only extremely long runs would yield any measurable amount of clinochlore. At lower pressures clinochlore did not form. (See data on the composition 5:1:3, reaction 14, Table 1.) Compositions in the high-alumina corner of the field at relatively high temperatures (see Table 1, reaction 10, compositions 26:42:32, 12:44:44 and 4:5:2) yielded cordierite and corundum as a stable pair at pressures of about 8,000 psi or greater. At lower pressures the results were not consistent, but mullite and spinel were formed more commonly. The possibility remains that extended periods of hydrothermal treatment under low pressure would bring about a transformation attributed to high pressure, but the time required would be beyond reason, experimentally. Nevertheless, evidence points to the favored formation of one assemblage at the expense of another at higher pressures. Furthermore, the role of water pressure may be particularly significant at decreasing temperatures, where a threshold value of activation energy may not have been attained to carry out a given reaction.

Apart from increasing the *rate* of some reactions, it has been found that with one or two notable exceptions, that the dT/dP or effect of pressure on the equilibrium temperature for a reaction (at a certain pressure) is quite low in systems such as the present in the range 5,000 psi to 30,000 psi. Furthermore, it is necessary also to consider whether the total pressure is equivalent to the water pressure and whether "directional" pressure has any different effect from that of hydrostatic pressure.

Discussion of Triangles. The series of triangles of Fig. 3 is our best interpretation of the available data for this system. Particularly at lower temperatures the data are sketchy, and many of the equilibria are represented by dashed lines, where suggested compatibility triangles have been extrapolated from known relations. The triangles represent divariant equilibria with three crystalline phases in equilibrium with water, and the transition indicated by the change from one set of the triangles to the next may be represented by a univariant pressure-temperature curve along which four phases are in equilibrium with H_2O . The temperature for each transition is given for a constant pressure of 10,000 psi but for most of the equilibria, pressure within the limits studied (2,000–20,000) had little ($< \pm 10^\circ$) effect on the transition temperatures. The reactions which indicate the transition from one set of triangles to the next are summarized as follows, and this order is used in summarizing the data in Table 1:

1. Gibbsite \rightleftharpoons boehmite + H_2O
2. Magnesium montmorillonite \rightleftharpoons talc + H_2O
3. Boehmite \rightleftharpoons diaspore
4. Spinel + H_2O \rightleftharpoons brucite + diaspore
5. Kaolinite \rightleftharpoons hydralite + aluminum montmorillonite + H_2O
6. Diaspore \rightleftharpoons corundum + H_2O
7. Aluminum montmorillonite \rightleftharpoons pyrophyllite + hydralite + H_2O
8. Serpentine + brucite \rightleftharpoons forsterite + H_2O
9. Montmorillonite \rightleftharpoons pyrophyllite + hydralite + H_2O + AS
10. Hydralite + pyrophyllite + AS (aluminian serpentine) \rightleftharpoons cordierite + H_2O
- 10a. Serpentine \rightleftharpoons forsterite + talc + H_2O
11. AS + brucite \rightleftharpoons forsterite + spinel + H_2O
12. Pyrophyllite \rightleftharpoons quartz + mullite + H_2O
- 12a. Brucite \rightleftharpoons periclase + H_2O
13. Talc + forsterite \rightleftharpoons enstatite + H_2O
14. Clinocllore \rightleftharpoons cordierite + forsterite + spinel + H_2O
15. Talc \rightleftharpoons enstatite + quartz + H_2O

Triangle 1 suggests relations below 130° C. where gibbsite is the stable alumina hydrate (see Ervin and Osborn (1951)). Montmorillonite is shown to cover a large field, presumably clear to the magnesia-silica boundary, although the evidence for the existence of a pure magnesia-

silica montmorillonite is not as positive as desired, as discussed under the the section on synthesis of montmorillonite.

In *Triangle 2* gibbsite has been replaced by boehmite, and the rest of the equilibria probably remain the same. Within this temperature region also the transition, $endellite \rightleftharpoons halloysite + H_2O$ takes place, but this has been described by Roy and Osborn (1952*a*, 1954) and a separate triangle is omitted for simplicity.

Triangle 3 describes the decrease in area of the montmorillonite field, and the pure magnesia-silica montmorillonite is replaced by talc. Data which suggest this transition are given in Table 1, reaction 2.

Triangle 4 represents the replacement of boehmite by diaspora (see Ervin and Osborn (1951)). A pressure of 2,000 psi or greater is believed necessary for the equilibrium existence of diaspora, one of the few reactions in which pressure up to 30,000 psi has been demonstrated to play a decisive role. The rest of the equilibria remain about the same. Within this temperature range there is evidence for the existence of the join, aluminian serpentine-diaspora for compositions in the high-alumina corner yield mixtures of an alumina mono-hydrate* and aluminian serpentine.

Triangle 5 describes the relations with spinel entering the equilibria. The temperatures for the reaction, $brucite + diaspora \rightleftharpoons spinel + H_2O$, 365° C. is taken from the system $MgO-Al_2O_3-H_2O$ (Roy, Roy and Osborn, 1953). Evidence for the existence of a join, spinel—AS (clinocllore composition) is found in mixtures with the following compositions: 75:15:10 and 70:15:15, which yield the three phases, brucite-AS-spinel, the aluminian serpentine having a basal spacing very close to that formed from the 5:1:3 $MgO:Al_2O_3:SiO_2$ composition. On the other hand, mixtures in the high-alumina region yield aluminian serpentine with a smaller spacing, corresponding possibly to the amesite composition; hence, an additional join is shown between aluminian serpentine (amesite composition) and diaspora (or boehmite). The montmorillonite field is shown to be smaller than in *Triangle 4*, (since certain mixtures do not yield at this temperature a single montmorillonite phase) although further intensive study would be necessary to precisely delineate the field at several specific temperatures.

In *Triangle 6* kaolinite is no longer stable, and is replaced, probably for an interval of about 15° C., by Al-montmorillonite + hydralsite + water

* In this study, as in the study of Ervin and Osborn (1951) and Roy, Roy and Osborn (1953) diaspora growth took place within its stability range only in the presence of seed crystals, or else with very long runs or at high pressures (20,000 psi). Therefore in most unseeded runs, boehmite was the alumina monohydrate encountered.

(see Table 1, reaction 5). Mixtures in the quaternary system containing appreciable MgO yield the assemblage, montmorillonite (Al, Mg) + hydralsite + aluminian serpentine (probably near the amesite composition) + H_2O .

In *Triangle 7* the equilibria are essentially the same as in *Triangle 6*, with diaspore replaced by corundum (see Ervin and Osborn (1951)). Considerable difficulty was encountered in establishing the significance of this transition in the ternary system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, because the presence of SiO_2 tends to inhibit the transition, $\text{diaspore} \rightleftharpoons \text{corundum} + \text{H}_2\text{O}$.

Triangle 8 describes the relations where pure Al-montmorillonite is no longer stable (Roy and Osborn, 1952a, 1953), but gives rise to pyrophyllite + hydralsite + H_2O . As previously discussed, the true stability range of hydralsite has not been definitely established but recent data suggest that the maximum "stability" temperature is about the same as, or slightly lower than that of pyrophyllite. In the event it is proven that hydralsite is only metastable, the above assemblage would be replaced by pyrophyllite + andalusite (or mullite) + H_2O . The establishment of an equilibrium relationship between hydralsite and andalusite would be particularly significant. The composition of hydralsite has not been precisely established, but is believed to be close to $2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ (see Roy and Osborn, 1952a, 1954). If this is the true composition of hydralsite, andalusite cannot exist in equilibrium with H_2O within the range where hydralsite is a stable phase; and even if the $\text{Al}_2\text{O}_3\text{:SiO}_2$ ratio in hydralsite is slightly different from 1:1, joins between this and other phases in the system may prevent the existence of the join, andalusite- H_2O . Such an occurrence would explain the difficulty in achieving the synthesis of andalusite.

Triangle 9 represents the replacement of serpentine + brucite by forsterite + H_2O . This reaction is described by Bowen and Tuttle (1949). Within this temperature range clinochlore has been synthesized at the expense of aluminian serpentine, and probably is the more stable phase (see Table 1, reaction 14, runs 5257, 5258 and 5294). It is not known whether or not clinochlore is stable at much lower temperatures, since the time required to bring about the formation of clinochlore increases greatly with decrease in temperature. The equilibria involving alumina are not very definite, since clinochlore has not been crystallized from high-alumina compositions; but inasmuch as aluminian serpentine of the clinochlore composition is considered to be metastable with respect to clinochlore within this temperature range, aluminian serpentine higher in Al_2O_3 is also presumed to be metastable. Joins connecting compatible phases are therefore drawn from the clinochlore composition.

In *Triangle 10* the magnesia-alumina montmorillonites are no longer

stable, giving rise instead to talc+pyrophyllite+AS+ H_2O , or pyrophyllite+AS+hydralsite (or andalusite)+ H_2O (see Table 1, reaction 9). Within this temperature range, as in the previous triangle, aluminian serpentine of the clinochlore composition is probably metastable. Thus, the equilibria are represented as involving clinochlore *or* aluminian serpentine, although in most runs aluminian serpentine was the phase encountered. A unique phase of the clinochlore composition was indicated as the stable phase for simplicity because no evidence for the *stability* of a chlorite or aluminian serpentine of higher Al_2O_3 content was obtained. (See Nelson and Roy (1953) for a later discussion.)

In Triangle 11 cordierite is stable in the presence of excess H_2O , although it may be stable at lower temperatures in the water-deficient region. Considerable time is necessary to form cordierite near its lower temperature limit, and therefore, the temperature for this reaction has not been located very accurately, about $500 \pm 25^\circ C$. (see Table 1, reaction 10). Decomposition of synthetic cordierite was effected as high as $475 \pm 20^\circ C$., but this is unfortunately about the upper temperature limit of the grinding apparatus. Synthesis of cordierite was achieved as low as $515 \pm 10^\circ C$. although in most runs near this temperature considerable amounts of non-equilibrium phases were still present. (For a comparison of the results of cordierite synthesis attempts at higher temperatures using different starting materials, see Table 2.) The triangles suggesting compatibility of cordierite with other phases were not definitely established down to the temperature of reaction 10, but they are presumed to be identical with those at slightly higher temperatures.

It is possible that the equilibria proceed directly from Triangle 9 to 11, without the intermediate equilibria represented by Triangle 10. The interval between the upper stability temperature of magnesia-alumina montmorillonite and the lower stability temperature of cordierite is within experimental error, considering the sluggishness of reaction producing cordierite, and the ever-present tendency to form non-equilibrium phases.

Triangle 12 represents the replacement of the join, aluminian serpentine (or clinochlore) -brucite by forsterite-spinel (see Table 1, reaction 11). Compositions in the high-magnesia corner always yielded aluminian serpentine, rather than clinochlore, as one phase. The failure to crystallize clinochlore from mixtures in this area may be explained by sluggish reaction at such low temperatures (below $530^\circ C$.) so that the true equilibrium phase clinochlore is never obtained. The aluminian serpentine obtained from the 75:15:10 and 70:15:15 mixtures had lattice dimensions identical with that of the 5:1:3 composition.

In Triangle 12a pyrophyllite is no longer stable (Roy and Osborn,

1952a, 1954), but is replaced by cristobalite+mullite (or andalusite) +H₂O (see Table 1, reaction 12). Sufficient data to delineate a stability region for andalusite were not obtained, but from natural occurrences the stability of andalusite rather than mullite would be favored within this temperature range. Experimentally it was found that higher water pressure, and in some cases prolonged duration of the run favored the formation of andalusite.

In Triangle 13 the only change is the replacement of brucite by periclase+H₂O. The temperature of this reaction was taken from the ternary system MgO-Al₂O₃-H₂O (Roy, Roy and Osborn, 1953), and data given under reaction 12a (see Table 1) show that the temperature for this transition is not appreciably affected by the addition of SiO₂ to the ternary system. The temperature, 635° C. at 10,000 psi, changes considerably with change in pressure, but this would not affect other reactions, inasmuch as no other reaction involving brucite or periclase takes place within the temperature and pressure range investigated.

Triangle 14 shows the replacement of the join, forsterite+talc by enstatite+H₂O. The temperature for this reaction is taken from Bowen and Tuttle (1949), and no data conflicting with this were found. A separate triangle should probably be drawn for the reaction, talc+clinochlore \rightleftharpoons forsterite+cordierite+H₂O. This is discussed by Yoder (1952).

In Triangle 15 clinochlore is no longer stable, but gives rise to the assemblage, forsterite+cordierite+spinel+H₂O. Dashed lines are drawn to indicate assemblages which are apparently less stable, but yet form readily from compositions in this area. High pressures, and long duration of runs in general tend to form the assemblage, forsterite+cordierite+spinel (+H₂O). Here again the true role of pressure is questionable—it may serve only to increase the rate of reaction; but at low pressures <10,000 psi the above-mentioned presumably stable assemblage was never attained, even with duration of runs as long as 22 days (see Table 1, reaction 14).

Triangle 16 represents the replacement of talc by enstatite+quartz +H₂O. The temperature of this transition was taken from Bowen and Tuttle (1949), and data obtained in the present study are not in disagreement with this value. Within this temperature range, also, there is a strong tendency to form the assemblage enstatite-spinel-cordierite (see data Table 1, reaction 15). Higher pressure tends to form instead the apparently more stable assemblage, cordierite-forsterite-spinel; whereas pressures of 8,000 psi or less did not form this assemblage in runs as long as 6 days.

Another step is shown by Yoder (1952), at 830° C. in which an inversion of cordierite takes place to yield a high temperature polymorph,

α -cordierite, very similar in x-ray diffraction pattern and optical properties. This area was not investigated extensively in the present study.

GENERAL DISCUSSION

Montmorillonite Formation in the System

The equilibria in the system $MgO-Al_2O_3-SiO_2-H_2O$ are basic to the problems of montmorillonite formation, inasmuch as the common cations forming the octahedral and tetrahedral layers are present. Cations which commonly fill the base exchange position, however, are absent and Mg^{2+} or a magnesia-complex must be the exchangeable cation in most cases. Three types of montmorillonites have been synthesized, which are not common in nature: pure alumina-silica montmorillonite, pure magnesia-silica-montmorillonite, and magnesia-alumina-silica montmorillonites (having *no* other cations present in the base exchange position). At low temperatures presumably approaching atmospheric conditions, the montmorillonite field covers a large area (or volume in the tetrahedron).^{*} Montmorillonites are formed from alumina-silica mixtures of about 1:3 $Al_2O_3:SiO_2$ molar ratio. Substitution of Al^{3+} for Si^{4+} in the tetrahedral layer must take place to result in an unbalance in charge, giving rise to the base exchange properties, and the base exchange position must be filled by an alumina complex such as $Al(OH)_2+$ (see Roy and Osborn (1952*a*, 1954)). The markedly lower expansion (with ethylene glycol) of this structure (to 13 Å) may provide evidence for the influence of the tetrahedral seat of charge on the degree of expansion.

A poorly-formed structure, apparently closely related to the montmorillonites, was formed from pure-magnesia-silica mixtures of the 3:4 $MgO:SiO_2$ ratio at temperatures below 250° C. Such a structure has previously been reported (Strese and Hofmann, 1941) but only in the presence of Na^+ as a base exchange cation, not present in this study. A definite mechanism for the formation of such a structure is difficult to picture, since the base exchange essential in montmorillonite structures is attributed to unbalance in charge caused by substitution in either the tetrahedral or octahedral layers. It is not easy to show that a comparatively large, low charged ion such as Mg^{2+} would substitute for Si^{4+} in the tetrahedral layer of a clay. However, the occurrence of Mg^{2+} in tetrahedral coordination in glasses is not uncommon (Roy, 1950). Another possible explanation may be that in such a loose, imperfectly formed structure a cation deficiency exists in the octahedral layer,

^{*} Actually the variability of composition with respect to water content is not very great compared to the variability with respect to other components, and the volume is actually a nearly flat slab.

with the deficiency in charge supplied by the base exchange cation. The possibility also remains, however, that such an imperfectly formed structure is actually only metastable; that, given sufficient time, would convert to the more stable structure, talc.

Other features of the montmorillonites have been described in the section on montmorillonite synthesis. Magnesia-alumina-silica montmorillonites of widely variable composition have been formed, in which substitution giving rise to unbalance in charge may take place in either the octahedral or tetrahedral layer, or both. Mg^{2+} (or a hydrated complex) is the exchangeable base, which is not common in itself, since in natural montmorillonites relatively small cations do not ordinarily enter the base exchange position. The existence of these montmorillonites, and the alumina-silica montmorillonite (see Roy and Osborn, 1952*a*, 1954) demonstrates the fact that a stable montmorillonite structure may be formed through the mechanism of unusual types of substitution when the more common types are not possible. In order to obtain further evidence, attempts to synthesize a "pure" gallia-silica montmorillonite having presumably the same structure as aluminum montmorillonite were made (Roy and Roy, 1954) and were successful.

The facts that the montmorillonite field covers a large area in the $MgO-Al_2O_3-SiO_2-H_2O$ diagram, and the mineral is formed stably up to fairly high temperatures, (480° C.) are rather surprising, since montmorillonite is largely a sedimentary mineral, and less commonly of hydrothermal origin—but not present in rocks commonly attributed to metamorphic processes. The addition of K_2O to the system $MgO-Al_2O_3-SiO_2-H_2O$, however, would move such compositions out of the montmorillonite field to produce micas, or under other conditions feldspars; the same would be the case with the addition of Na_2O . The question of equilibrium co-existence of a mica and montmorillonite is quite intriguing from the clay mineralogist's viewpoint.

Clay Mineral Assemblages

Within this system are included representatives of each of the clay mineral groups, and the addition of several mole per cent of potash would enable us to very closely duplicate compositions of a high proportion of clay-bearing rocks.

The montmorillonites are seen in this presentation to completely dominate the picture, so that only in a small area of the system do we not have montmorillonite as *one* of the phases formed. The mode of representation, however, somewhat over-emphasizes the position of the montmorillonites. If the projection had been made on the $Al_2O_3-SiO_2-H_2O$ face the position of kaolinite would also have been striking. However, one

of the main reasons for the abundance of kaolinite in nature is that a large fraction of these clays is secondary and derived from weathering of feldspars and micas, and even rocks containing a very low percentage of magnesium. The relatively pure primary kaolinites not contaminated by phases other than alumina-hydrates must also be ascribed to a relatively "pure" (Mg-free) source area. Under all other conditions one would expect montmorillonite to be present in significant amounts. The lowest temperature triangle would imply that kaolinite-montmorillonite mixtures should not be very common in primary sedimentary deposits. On the other hand one would expect a fairly common occurrence of montmorillonites with the 7 Å (or 14 Å) chlorites, represented respectively, by aluminian serpentine and clinochlore. These low temperature triangles (1-5) also indicate (though unfortunately at these temperatures it is nearly impossible to claim that equilibrium has been attained) that the 7 Å kaolinite and 7 Å aluminian-serpentine are incompatible and that a more common assemblage would involve either of these 7 Å phases with boehmite (or gibbsite) and montmorillonite. Triangles such as 5 and 6 show that these clay mineral phases will persist to quite high temperatures (well into the metamorphic range) and indeed, the assemblage, chlorites-montmorillonites covers a large area of the compositional field. In nature the presence of K^+ transforms many of the montmorillonites into micas. It is nevertheless a remarkable fact that a montmorillonite is actually stable up to 480° C.

It is worthy of note that no case of "interlayering" effects was noticed on the *x*-ray patterns. The so-called mixed-layer phases (giving "interfering" *x*-ray patterns) composed, at least, of any combination of the phases kaolinite, montmorillonite, and chlorite (including 7 Å aluminian serpentines) must therefore be metastable assemblages which are mixtures of two phases within the context of the phase rule.

The Stability of Andalusite

Andalusite was synthesized apparently for the first time in the present study (see Roy, 1953) and its stability has been discussed also in part under the Discussion of Triangles. General difficulties arising in attempts to synthesize the aluminosilicates have been described by Roy and Osborn (1951, 1953). In the present study only suggestions of a stability region for andalusite have been obtained although the synthesis was achieved reproducibly. Several inter-related factors influence the delineation of a stability range for andalusite.

First, andalusite cannot be stable in the presence of excess water below about 400° C., inasmuch as the hydrates, diaspore and kaolinite are stable and compatible up to this temperature. In the presence of a defi-

ciency of H_2O , andalusite may be stable to low temperatures, although the slow rate of reaction at these temperatures will be an important factor in the experimental determination of a lower temperature limit under these conditions.

Second, another hydrous aluminosilicate, hydralsite, has about the same alumina-silica ratio as andalusite. The stability range of this structure has not been definitely established, but most recent indications are that it may be about as high as that of pyrophyllite ($575^\circ\text{C}.$). Andalusite has in some cases been synthesized as low as $450^\circ\text{C}.$, with fairly long duration of run and relatively high water pressures. From the compositional limitations it would be very unlikely that both structures are stable in the presence of excess H_2O in the same temperature and pressure range. Decomposition of hydralsite to yield andalusite + H_2O would be a positive indication both of a maximum stability temperature for hydralsite and a minimum for andalusite (in the presence of excess H_2O). But it has not been possible as yet to achieve such a reaction.

Third, the presence of certain impurities apparently facilitates the synthesis of andalusite. The synthesis was achieved only with great difficulty, and in the presence of andalusite "seeds," from pure Al_2O_3 - SiO_2 mixtures,* while in the presence of small amounts of MgO , or starting with natural slightly impure kaolinites synthesis was achieved more readily.

The effect of the presence of impurities such as Mg^{2+} may also be explained on the basis of the favorable coordination conditions (6 fold) that Mg^{2+} ions would prefer. On this basis also both $(\text{OH})^-$ and F^- ions will make it easier to form these aluminosilicate structures if they enter them. The presence of impurities may be of considerable importance when attempting to correlate experimental equilibrium data with natural occurrences, to obtain a better picture on the stability of andalusite, since in nature a host of "impurities" are available. One hopeful feature is the fact that the highest stability of a hydrate mineral in the portion of the system in which the aluminosilicates are involved is $575^\circ\text{C}.$ (pyrophyllite), and hence extended investigation by hydrothermal techniques has a possibility of yielding further information on the stability of the anhydrous aluminosilicates, which in turn may be correlated with natural mineral associations. The present position on the anhydrous aluminosilicates is therefore not much advanced over much earlier work. The data indicate that mullite is the stable aluminosilicate at pressures below say 30,000 psi from $575^\circ\text{C}.$ upwards and probably as

* Experimentally other factors such as the state of starting material were of considerable significance, but these should not affect the ultimate equilibria.

low as 400° C. In this pressure range the only possible change may be that it is metastable from 575–400° and andalusite is stable with corundum. Of course, it is not impossible that andalusite and mullite be both stable at low pressures.

The Stability of Cordierite—Corundum or Spinel—Mullite

One of the more remarkable features of the equilibria determined in the high-alumina portion of the system is the apparent compatibility of cordierite and corundum. At solidus temperatures in the system $MgO-Al_2O_3-SiO_2$, spinel and mullite coexist, but the data obtained in the present study (see Table 2, esp. reaction 10) strongly suggest that cordierite and corundum are compatible, at least below about 800° C.

The pair mullite-spinel is sometimes formed in runs of relatively short duration, whereas cordierite-corundum is formed under prolonged hydrothermal treatment; and at lower H_2O pressures, where presumably the solubility of the phases is lower and reaction would take place more slowly, the pair mullite-spinel is sometimes formed, whereas cordierite-corundum is formed almost invariably at higher pressures. The second factor suggests that a minimum pressure may be required for the formation of the assemblage, cordierite-corundum; and, indeed, it is recognized that spinel and mullite are compatible in the sanidinite facies, characterized by high temperatures and low pressures. Metamorphic field assemblages (Tilley, 1924) suggest, however, that cordierite and corundum are compatible under the conditions characteristic of the pyroxene-hornfels facies, presumably of lower temperatures and higher pressures. Extensive study, with the availability of new experimental techniques to attain higher temperatures under hydrothermal conditions might yield some information on the existence of a pressure-temperature curve for the reaction $spinel + mullite \rightleftharpoons cordierite + corundum$.

The Joins Forsterite-cordierite and Enstatite-spinel

At solidus temperatures in the system $MgO-Al_2O_3-SiO_2$, the phases, forsterite, cordierite and spinel coexist at equilibrium. These three phases are also apparently compatible in equilibrium with H_2O above 680° C. at 15,000 psi (Yoder, 1952). In the present study repeated runs at pressures of 10,000 psi or lower yielded evidence suggesting that the joins, enstatite-spinel and talc-spinel are stable. The assemblage, cordierite-enstatite-spinel appeared to be stable above 725° C. with prolonged runs at 10,000 psi; whereas at 20,000 psi similar runs yielded, cordierite-forsterite-spinel. Spinel-cordierite-hypersthene associations in nature (approximated by spinel-cordierite-enstatite) are typical of the pyroxene-hornfels facies (Tilley, 1924), rather than the assemblage,

spinel-forsterite-cordierite. The fact that spinel-forsterite-cordierite is obtained stably at the solidus temperature under atmospheric pressure and also apparently stably at lower temperatures (above about 700° C. at 20,000 psi) at high pressures would indicate that it is unlikely that the alternative assemblage, spinel-enstatite-cordierite is stable in the same temperature range under intermediate pressures. This is not positive evidence that the assemblage, spinel-enstatite-cordierite is formed only metastably, but does suggest a mechanism for its formation in nature.

SUMMARY AND CONCLUSIONS

Phase equilibria in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ have been determined by hydrothermal techniques. At the highest temperatures studied (above about 800° C. at 10,000 psi) only anhydrous minerals are stable, and the equilibria are expressed in terms of compatibility triangles of three phases in equilibrium with H_2O , differing in only a few instances from the "condensed" equilibria in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. A notable exception is the existence of the cordierite-corundum join, rather than the join, spinel-mullite. No evidence for the presence of sillimanite, andalusite or kyanite was obtained at these temperatures and pressures.

With decreasing temperature hydrated minerals enter the equilibria — first talc, at 780° C. and 10,000 psi—and then below 700° C. at 20,000 psi the first quaternary phase, clinocllore is stable. An interesting polymorphism is observed between clinocllore and "aluminian serpentine" of the same composition. A definite p - T curve for the transformation could not be determined because of the sluggishness of reaction, but higher pressures and temperatures were found to favor the formation of clinocllore. The hydration of periclase to brucite takes place at 635° C. at 10,000 psi, the temperature of the reaction changes considerably with variation in pressure. Within the smaller tetrahedron, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$, the highest hydrate stability is that of pyrophyllite (575° C. at 10,000 psi); the upper stability temperature of hydralsite ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$), a micaceous type phase, does not exceed this temperature. Andalusite was synthesized at temperatures between about 450° C. and 700° C., but no definite stability range could be established on the basis of the data obtained.

Cordierite is no longer stable in the presence of excess H_2O below about 500° C., and the character of the equilibria is changed considerably by its disappearance. Another quaternary phase, montmorillonite, of variable composition enters the equilibria below about 480° C., and its stability field covers a large area at lower temperatures. Alumina hydrates, in place of corundum, are formed below about 400° C., at which tempera-

tures kaolinite is also stable. Below about $365^{\circ}C$., spinel ($+H_2O$) is replaced by brucite+diaspore (or boehmite); i.e., spinel is no longer stable in the presence of excess H_2O . At lowest temperatures a magnesia-silica montmorillonite phase is formed at the expense of talc, in addition to the quaternary montmorillonites, which cover a large field.

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to Dean E. F. Osborn for his suggestions and help throughout the study, and for general supervision of the research project as well as for his critical reading of the manuscript. The larger part of the research was carried out under the sponsorship of the Office of Naval Research, Project No. *N6onr-26909*.

REFERENCES

- BALCONI, M. (1941), Synthesis of sillimanite: *Rend. Soc. Min. Ital.*, **1**, 77.
- BOWEN, N. L., AND GREIG, J. W. (1924), The System $Al_2O_3-SiO_2$: *J. Am. Cer. Soc.*, **7**, No. 4, 238-254; and *ibid.*, No. 5, 410.
- BOWEN, N. L., AND TUTTLE, O. F. (1949), The System $MgO-SiO_2-H_2O$: *Bull. Geol. Soc. Am.*, **60**, 439-460.
- FOSTER, W. R. (1950), Synthetic sapphirine and its stability relations in the system $MgO-Al_2O_3-SiO_2$: *J. Am. Cer. Soc.*, **33**, 73-84.
- GREIG, J. W. (1927), Immiscibility in silicate melts, I-II: *Am. J. Sci.* (5th Ser.), **13**, (73), 1-44; and (74), 133-154.
- KEITH, M. L., AND SCHAIRER, J. F. (1952), The stability field of sapphirine in the system $MgO-Al_2O_3-SiO_2$: *Jour. Geol.*, **60**, 181-186.
- KENNEDY, G. D. (1950), Pressure-volume-temperature relations in water at elevated temperatures and pressures: *Am. J. Sci.*, **248**, 540-564.
- MICHEL-LEVY, M. C. (1950), Reproduction artificielle de la sillimanite: *Compt. Rend.*, **230**, 2213.
- MOREY, G. W. (1942), Solubility of solids in water vapor: *Proc. Am. Soc. Testing Materials*, **42**, 986.
- MOREY, G. W., AND INGERSON, E. (1937a), Pneumatolytic and hydrothermal synthesis of silicates: *Econ. Geol.*, **32**, 607-761.
- (1937b), A bomb for use in hydrothermal experimentation: *Am. Mineral.*, **22**, 1121-1122.
- NELSON, B. W., AND ROY, R. (1953), Structural-chemical classifications of the chlorites: Magnesian chlorites. Presented at Geological Society of America Annual Meeting, Toronto, November 1953.
- RANKIN, G. A., AND MERWIN, H. E. (1918), The ternary system $MgO-Al_2O_3-SiO_2$: *Am. J. Sci.*, 4th Ser., **45**, 301-325.
- ROY, D. M. (1952), Phase equilibria in the system $MgO-Al_2O_3-H_2O$ and in quaternary systems derived by the addition of SiO_2 , CO_2 and N_2O_5 . Ph.D. Dissertation, The Pennsylvania State University, January 1952.
- ROY, D. M. (1954), The hydrothermal synthesis of andalusite: *Am. Mineral.*, **39**, 140-143.
- ROY, D. M., ROY, R., AND OSBORN, E. F. (1953), The system $MgO-Al_2O_3-H_2O$ and the influence of carbonate and nitrate ions on the phase equilibria: *Am. J. Sci.*, **251**, 337-361.

- ROY, D. M., AND ROY, R. (1952), Studies in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$: *Bull. Geol. Soc. Am.*, **63**, 1293 (Abstract).
- ROY, D. M., AND ROY, R. (1954), An experimental study of the formation and properties of synthetic serpentines and related layer silicate minerals: *Am. Mineral.*, **39**, 957-975.
- ROY, R. (1950), Magnesium in fourfold coordination in glass: *J. Am. Chem. Soc.*, **72**, 3307.
- ROY, R. (1953), Application of phase equilibrium data to certain aspects of clay mineralogy. Presented at 2nd National Clay Conference, Columbia, Mo., October 1953.
- ROY, R., AND OSBORN, E. F. (1952a), Studies in the system alumina-silica-water. Problems of clay and laterite genesis symposium: *Am. Inst. Min. Met. Eng.*, 76-80.
- (1952b), Some simple aids in the hydrothermal investigation of mineral systems: *Econ. Geol.*, **47**, 717-721.
- , (1954), The System, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *Am. Mineral.*, **39**, 853-885.
- STRESE, H., AND HOFMANN, U. (1941), Synthesis of magnesium silicate gels with two-dimensional structure: *Zeit. anorg. allgem. Chem.*, **247**, 65-95.
- TUTTLE, O. F. (1948), A new hydrothermal quenching apparatus: *Am. J. Sci.*, **246**, 628-635.
- YODER, H. S. (1952), The $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system and the related metamorphic facies: *Am. J. Sci.*, *Bowen Vol.*, 569-627.

Manuscript received March 20, 1954.

SIMPLE METHOD FOR THE DETERMINATION OF THE PLAGIOCLASE FELDSPARS

WILFRID R. FOSTER,

College of Engineering, Ohio State University, Columbus 10, Ohio.

ABSTRACT

Precise refractive index data on synthetic plagioclase feldspar glasses have been available for over forty years. However, no routine method based upon these data has come into general use for the determination of the natural feldspars. Such a method possesses certain advantages over the many other procedures presently followed. Its theoretical accuracy is about twice that obtainable with established refractive index methods. Index determinations, involving no particular refinements of technique, were made on the glasses of ten chemically analyzed natural plagioclase feldspars. The anorthite contents derived from these data agreed with those calculated from the chemical analyses within about two per cent. The method is simple and rapid, and calls for no costly equipment; some platinum foil for enclosing the feldspar sample, and a blowpipe capable of yielding a 1550° C. flame, are the only "extras" needed. It is therefore recommended for inclusion among the standard methods for the determination of the plagioclase feldspars.

INTRODUCTION

Numerous methods are available whereby the composition of the plagioclase feldspars may be determined by the measurement of various physical properties (1) (2) (3). Poldervaart (4) has recently discussed the advantages and limitations of many of the standard methods. It is generally recognized that no single method is universally applicable, and that the determinative charts presently available are not entirely adequate. New techniques continue to be devised, such as the x-ray diffraction method recently proposed by Claisse (5). In view of the great importance to the petrologist of accurate plagioclase determination, further developments in this field are to be expected.

In 1909 Larsen (6) recorded the refractive indices of six pure synthetic glasses of the albite-anorthite series. Four years later Bowen (7) utilized these data to locate several liquidus points on the now-famous phase-equilibrium diagram of the plagioclase feldspars. Little if any determinative use has since been made of Larsen's data, and the possibilities of the feldspar glasses in analytical work, thus early recognized by Bowen, have been subsequently neglected. With the exception of the specific gravity curve presented by Poldervaart (4), no curves for the physical properties of the glasses have ever appeared among the determinative charts of the plagioclase series. Whereas refractive index curves for the crystalline feldspars have been widely used in determinative work, the curve derivable from Larsen's refractive index data for the feldspar glasses has never been recommended for similar use.

To the writer it appeared that the excellent agreement obtained by

Bowen between optical and thermal determinations in the laboratory system augured well for the usefulness of glass indices in routine analyses of the natural plagioclases. Before advocating its general use for such a purpose, however, it was considered advisable to test the method on natural analyzed feldspars, while employing a technique of glass-formation readily accessible to the average petrographer. A suite of eight analyzed feldspars previously studied by Meen (8) was made available to the writer, and was used in preliminary tests. The bulk of the determinations were made on ten analyzed feldspars furnished by N. L. Bowen, and for which chemical analyses have been presented by Kracek and Neuvonen (9).

DETERMINATIVE PROCEDURE

The basis of the proposed method is the data previously provided by Larsen (6). The lowermost curve of Fig. 1 is a plot of these data. For

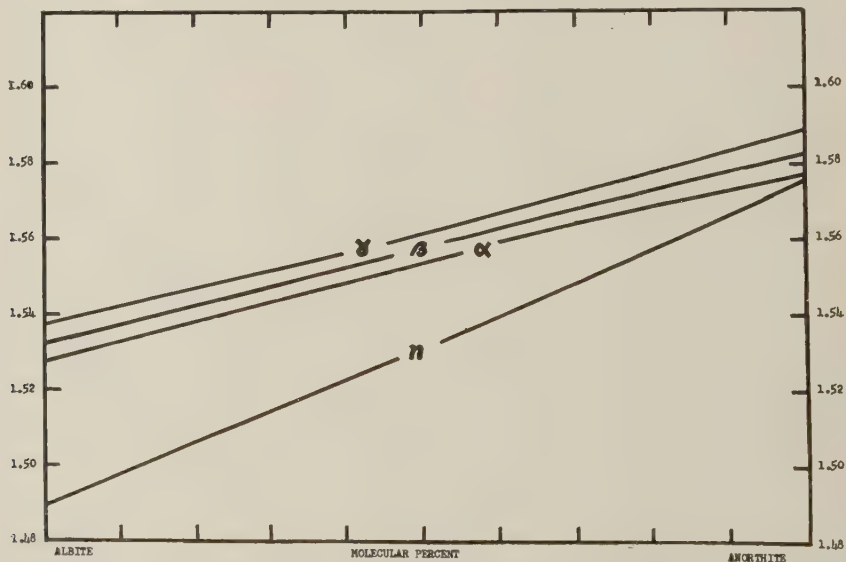


FIG. 1. Refractive indices of the plagioclase feldspars. Lower curve: feldspar glasses (after Larsen). Upper curves: crystalline feldspars (after Kennedy).

comparison, curves for the three principal indices of the crystalline feldspars, after Kennedy (10), are also included. In accordance with almost universal practice, these data have been plotted on a molecular basis. It is recommended that for determinative use the vertical scale be increased by a factor of 2:1 over that shown in the illustration. For the convenience

of the reader who wishes to prepare his own working-curve the required data, after Larsen (6), are presented in Table 1.

The procedure involved in obtaining the feldspar glasses is simple and rapid. A "pinch" of feldspar powder, or a tiny sliver, is wrapped in a small piece of thin platinum foil and held for several minutes in the hottest flame of the blowpipe. An oxygen-gas blowpipe is much to be preferred over the ordinary mineralogical blowpipe, because of greater convenience of operation, and of the ready attainment of melting temperatures as high as 1550° C. The heat-treated platinum-wrapped sample is plunged directly into water, in order to quench the molten charge to a glass. Although unnecessary for the albitic feldspars, this precaution is required in the case of the anorthite-rich feldspars, if recrystallization is

TABLE 1.

<i>Molecular Composition</i>	<i>Refractive Indices of Glasses</i> (sodium light)
Ab (100%): An (0%)	1.4890
Ab (66⅔%): An (33⅓%)	1.5166
Ab (50%): An (50%)	1.53075
Ab (33⅓%): An (66⅔%)	1.5452
Ab (16⅔%): An (83⅓%)	1.5600
Ab (0%): An (100%)	1.5755

to be avoided. The glassy charge is then broken free of its platinum wrapping, and its refractive index is measured with the aid of a reliable set of standardized immersion media. The immersion oils used in this study were separated by index-increments of 0.005. If employed at some temperature other than that at which they were standardized, the oils should be re-calibrated with the aid of a refractometer during use, or a suitable temperature-correction should be applied. Sodium light is recommended as the illumination-source. The refractive index of the glass is easily estimated to the nearest 0.001 of index. The anorthite content is then estimated, to the nearest 0.5%, from the appropriate refractive-index curve. Further refinement of technique, such as that involved in the double-variation method of Emmons (11), would doubtless enhance the accuracy obtainable with the procedure described above. For present purposes, however, it seemed preferable to outline a routine method which might be utilized in even the most modestly-equipped petrographic laboratory.

RESULTS

The results of duplicate determinations on glasses of each of the ten analyzed feldspars furnished by Bowen are presented in Table 2.

TABLE 2. ANORTHITE CONTENTS OF 10 ANALYZED NATURAL PLAGIOCLASE FELDSPARS

*Number of Sample	Molecular Percentages from Chemical Analyses			Molecular Percentages from Indices of Glasses	
	% Or	% Ab	% An	% An(I)	% An (II)
13	0.7	98.7	0.6	0.0	0.0
8	1.3	81.9	16.8	17.5	17.5
10	3.9	74.5	21.6	20.5	21.5
6	2.4	45.7	51.9	50.0	51.0
7	1.2	35.0	63.8	63.0	62.0
5	(trace)	30.3	69.7	70.5	70.0
4	1.0	23.0	76.0	75.5	75.5
3	0.5	19.5	80.0	79.5	80.0
2	0.3	13.9	85.8	85.0	84.5
1	0.3	7.1	92.6	93.5	93.0

* Sample numbers are from Tables 1 and 3, Kracek and Neuvonen (9).

In the above table are included also the proportions of the orthoclase, albite and anorthite components calculated from the chemical analyses (9). In this calculation the assumption has been made that each of the oxides, K_2O , Na_2O , and CaO , is wholly confined to the Or, Ab, and An components, respectively.

It is apparent from an examination of Table 2 that the anorthite contents experimentally determined from the refractive index measurements are in reasonably good agreement with those calculated from the chemical analyses. Larsen, Irving, Gonyer, and Larsen (12) considered their determination of plagioclase feldspars of the San Juan, Colorado, volcanics to be correct to within $\pm 3\%$ of the anorthite content. Poldervaart (4) has recently stated that the plagioclase series is normally determined optically with an accuracy of $\pm 2\%$. A comparable accuracy is indicated for the method under discussion.

DISCUSSION OF METHOD

Many of the standard methods of plagioclase determination suffer from the drawback that ambiguous results are given for certain portions of the composition range. Even the method based upon the refractive indices of the crystalline feldspars is not free from this defect. The index-curves presented by different authorities often show significant differ-

ences. Then too, the selection of one of the three principal indices, or of a specific intermediate index, is attended with some uncertainty. The presence of zoning, or of intimate exsolution-intergrowths of two feldspars of different composition, poses the question as to whether the grain or grains measured are representative of the average plagioclase composition. Poldervaart (4) proposed to overcome the difficulty of strong zoning, by forsaking optical methods entirely in favor of a mean specific gravity test on the feldspar powder. But this does not appear to be too satisfactory a solution to the problem, in the light of the results of Meen (8). He found that, in spite of careful separation, his purified feldspars contained inclusions which materially affected the specific gravity measurements. Indeed, two feldspars shown by Meen to differ by as much as 23% in anorthite content were found by him to have closely similar specific gravities. The presence of the orthoclase component in solid solution is believed by some to have a substantial effect on the feldspar optics (8). A further complication in feldspar determination is inserted by the recent recognition of high- and low-temperature feldspars of identical composition, yet different optical constants (13, 14). All of these factors conspire to render determinations based on standard refractive index curves of doubtful accuracy.

The simple method herein proposed is free of most of the defects enumerated above. Uncertainty due to possible misinterpretation of the orientation of the measured grain is eliminated. There is but a single index to be measured on the feldspar glass, regardless of grain-orientation. Comparison of the lower curve of Fig. 1 with the upper trio of curves in the same figure readily reveals the greater determinative accuracy of the former. The difficulties introduced by zoning and unmixing of feldspars are also surmounted in the present method. Thus, in preparing the feldspar glass it is possible to employ a sample involving hundreds of grains. Any inhomogeneity in feldspar composition in the original granular sample may be removed by repeated crushing and fusion, prior to index-measurement. A reliable value for the average plagioclase composition can thus be assured. And what about the possible effect of the orthoclase component present in solid solution in the plagioclase? In this connection it is to be noted that the refractive indices of the glasses of orthoclase and albite are almost identical: 1.487 and 1.489, respectively. The determination of the anorthite content of a feldspar glass would therefore be but little affected by the substitution of even substantial amounts of the orthoclase for the albite component. It is also immaterial whether the original crystalline feldspar exhibited a high- or a low-temperature form or both. In view of the advantages enumerated above, this simple method would certainly appear less precarious in the hands of the novice than presently accepted methods.

Probably the most severe criticism that can be levelled at the proposed method is that it calls for a reasonable degree of purification of the feldspar prior to fusion and index-measurement. However, this does not seem to be too serious an obstacle. The coarser specimens of feldspar will yield suitable material directly, without need for purification. Finely disseminated feldspar, however, requires a refining process. But even this need involve no more elaborate procedure than crushing, sorting, magnetic extraction, and suspension in bromoform suitably diluted with benzene, as proposed by Meen (8). The indications, too, are that a small amount of impurity is not too disturbing. It is common experience in silicate equilibrium research that homogeneous glasses approximating the feldspars are attained only after prolonged and repeated fusion. It is very doubtful that the short fusion time generally employed in the present method would permit appreciable diffusion of the impurities through the glass. It is therefore believed that only in the occasional case of repeated fusions, carried out to counteract zoning or exsolution effects, need the impurity factor cause concern. It was earlier remarked that two feldspars found by Meen (8) to differ by 23% in their anorthite contents yielded specific gravities which were roughly the same. Meen attributed these erratic specific gravity data to foreign inclusions. Yet in the present study the glasses of these two feldspars checked the anorthite contents calculated from their respective chemical analyses to within 2%. Apparently, impurities capable of invalidating specific gravity data as an analytical tool had no adverse effect in the determination of the anorthite contents by the glass-index method.

Another possible disturbing factor merits at least passing comment. It is well known that a glass may exhibit index-variations involving the fourth, and even the third decimal place, depending on its thermal history (15). A glance at Fig. 1 reveals that each 0.001 of index-variation would correspond to about 1% change in anorthite content. But fortunately it is only between the annealed and the un-annealed specimens of a given glass that substantial index-contrasts are displayed. Since the technique proposed in this paper involves quenched un-annealed glasses exclusively, no difficulty should be introduced by such a factor.

Why has this simple method been so long and so completely ignored, when every other possibility has been thoroughly scouted? In this connection it is to be recalled that Larsen's data (6) were obtained on glasses synthesized from the purest available chemicals. Their use by Bowen (7) likewise involved pure synthetic mixtures. There has always been some reluctance to assume that data obtained on pure laboratory melts are directly applicable to systems involving natural minerals.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Dr. V. B. Meen of the Royal Ontario Museum, and to Dr. N. L. Bowen of the Geophysical Laboratory, for supplying the analyzed feldspars used in this study. Dr. Bowen also kindly read the manuscript. The investigation was begun in the research laboratories of the Ceramic Division of the Champion Spark Plug Company, Detroit, Michigan. For the facilities and encouragement provided by Messrs. F. H. Riddle and H. F. Royal of that organization the writer is also grateful.

REFERENCES

1. JOHANNSEN, A. (1928), Essentials for the Microscopical Determination of Rock-forming Minerals and Rocks: 2nd Edition (University of Chicago Press, Chicago, Ill.), pp. 30-33.
2. ROGERS, A. F., AND KERR, P. F. (1942), Optical Mineralogy: 2nd Edition (McGraw-Hill Book Company, Inc., New York, N. Y.), pp. 238-251.
3. WINCHELL, A. N. (with collaboration of WINCHELL, H.) (1951), Elements of Optical Mineralogy. Part II. Descriptions of Minerals: 4th Edition (John Wiley & Sons, Inc., New York, N. Y.), pp. 261-302, 312-330.
4. POLDERVAART, A. (1950), Correlation of physical properties and chemical composition in the plagioclase, olivine, and orthopyroxene series: *Am. Mineral.*, **35**, 1067-1079.
5. CLAISSE, F. (1950), A roentgenographic method for determining plagioclases: *Am. Mineral.*, **35**, 412-420.
6. LARSEN, E. S., JR. (1909), The relation between the refractive index and the density of some crystallized silicates and their glasses: *Am. J. Sci.* (4), **28**, 263-274.
7. BOWEN, N. L. (1913), The melting phenomena of the plagioclase feldspars: *Am. J. Sci.* (4), **35**, 577-599.
8. MEEN, V. B. (1933), A description of a few plagioclases. Determination of specific gravity of minerals by use of index liquids: *Univ. of Toronto Studies, Geol. Series, No.* **35**, 37-45, 47-50.
9. KRACEK, F. C., AND NEUVONEN, K. J. (1952), Thermochemistry of plagioclase and alkali feldspars: *Am. J. Sci., Bowen Volume*, 293-318.
10. KENNEDY, G. C. (1947), Charts for correlation of optical properties with chemical composition of some common rock-forming minerals: *Am. Mineral.*, **32**, 561-574.
11. EMMONS, R. C. (1943), The Universal Stage: *Memoir 8, Geological Society of America*, pp. 55-101.
12. LARSEN, E. S., JR., IRVING, J., GONYER, F. A., AND LARSEN, E. S., 3rd (1938) Petrologic results of a study of the minerals from the Tertiary volcanic rocks of the San Juan region, Colorado: *Am. Mineral.*, **23**, 227-257.
13. CHAO, S. H., AND TAYLOR, W. H. (1940), Isomorphous replacement and superlattice structures in the plagioclase feldspars: *Proc. Royal Soc. London*, **176**, 76-87.
14. TUTTLE, O. F., AND BOWEN, N. L. (1950), High-temperature albite and contiguous feldspars: *J. Geol.*, **58**, 572-583.
15. WEYL, W. A. (1951), Phase Transformations in Solids; Chapter 11, Transitions in glass (John Wiley & Sons, Inc., New York, N. Y.), p. 326.

DIRECTIONAL GRINDING HARDNESS IN DIAMOND: A FURTHER STUDY*

REYNOLDS M. DENNING, *University of Michigan, Ann Arbor, Michigan.*

ABSTRACT

Additional results of measurements of directional relative grinding hardness of single crystal diamonds are given for selected planes. The dependence of relative grinding hardness of a given direction upon the position of the plane being ground is illustrated. The relation of grinding hardness to class symmetry is discussed.

In a previous paper¹ the results of the measurement of the relative grinding hardness in oriented planes on single crystal diamonds have been considered. The present paper deals with results of further work in five additional planes.

The experimental technique of the measurement of relative grinding hardness in single crystals has been briefly described in the above-mentioned paper. Essentially a grinding constant, K , the volume of material removed per unit time per unit thrust on a conventional diamond cutter's wheel, was determined simultaneously on two separate crystals for a reference direction and the direction under investigation. The relative grinding hardness is the ratio of the grinding constant of the specified direction with respect to that of the reference direction. In all cases the reference direction used was [100] in (001). In the present tests thrusts of two kilograms were maintained on the stones. The areas of the ground facets were between one-half and two square millimeters.

In zone [010] measurements on planes 5° and 38° from the cube plane are given. The zero azimuth for grinding directions in these planes is a direction toward the cube. For the plane 5° from the cube (Fig. 1), the maxima and minima are located as in the cube. It will be noted that the minimum at zero degrees represents a very hard direction, but that the minima at 90° and 180° represent relatively soft directions. It can be seen from the great changes in the magnitude of the zero degree minimum on this plane as compared with the cube that a very small orientation error on the cube may produce a large change in the relative grinding hardness so that unless a cube plane be oriented with high accuracy (a few minutes of arc) the characteristic four-fold symmetry of the hardness vectors on the cube will not be observed.

If it is assumed that the relative grinding hardness variation with re-

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 187.

¹ Denning, Reynolds M., Directional grinding hardness in diamond: *Am. Mineral.*, **38**, 108-117 (1953).

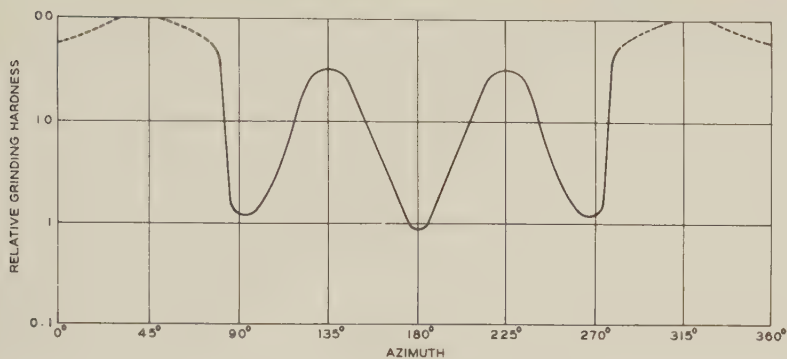


FIG. 1. Zone [010] 5° from cube.

spect to this misorientation is linear, then the rate of change of relative grinding hardness with respect to angular deviation is 20% per minute of arc. This high rate of change explains the extreme sensitivity of the symmetry of grinding rates with respect to small misorientations. With the exception of the great increase in relative grinding hardness in one sector, the curve rather closely resembles the curve for the cube face. The minimum at 180° seems to be a little lower than the corresponding point when the cube is being ground. Unfortunately, the difference lies at about the limit of accuracy of measurement so that this relation may not be significant.

A plane 38° from the cube (7° from the dodecahedron) in zone [010] exhibits the relative grinding hardness variation illustrated in Fig. 2. This plane shows hardness variation of the same order of magnitude as the dodecahedron. (The zero azimuth of the published dodecahedron curve²

² *Ibid.*, Figure 4.

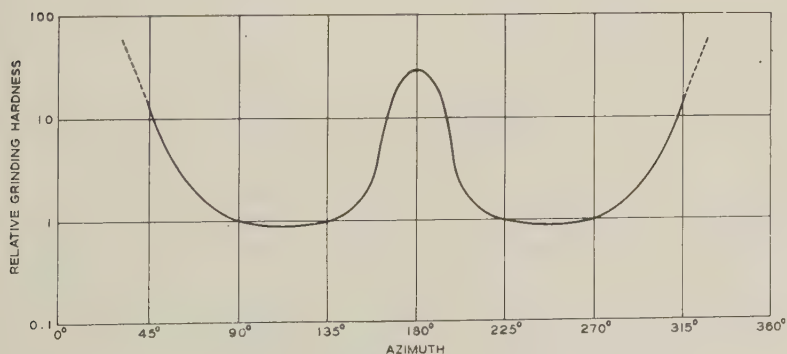
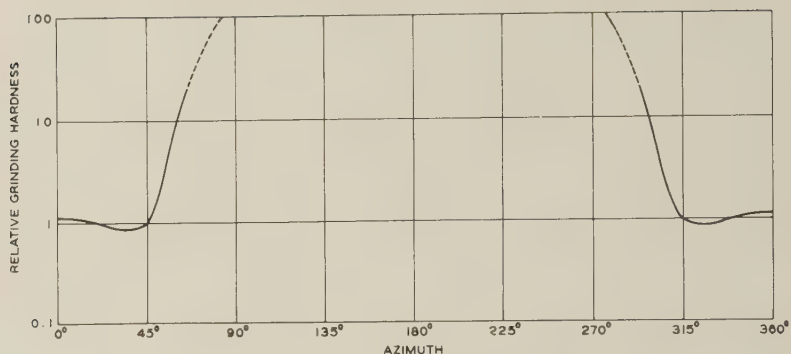
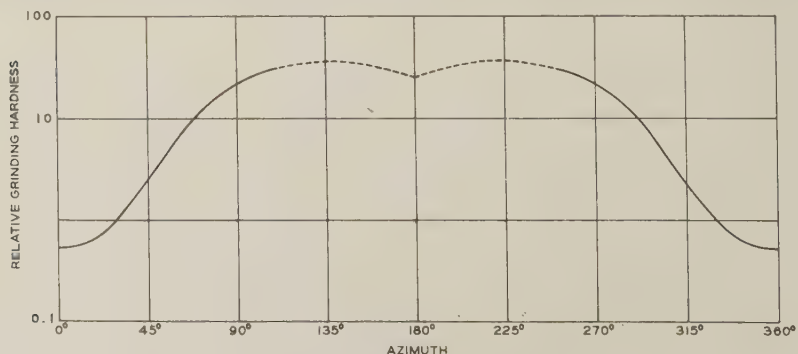


FIG. 2. Zone [010] 38° from cube.

FIG. 3. Zone $[\bar{1}01]$ 5° from dodecahedron.

is shifted 90° with respect to other planes in the zone $[010]$.) In the plane 38° from the cube, the hardness minimum is rather broad, covering two 45° sectors. From the shape of this curve it can be seen that small orientation errors of (101) are not serious in the determination of the hardness curve of the dodecahedron, provided that the plane being measured accurately lies in zone $[010]$. That such is not the case if the plane measured does not accurately contain the $[010]$ direction is illustrated by considering the next plane.

If a plane in zone $[\bar{1}01]$, 5° from the dodecahedron, be ground in a series of azimuths and the results plotted, a curve such as that of Fig. 3 is obtained. The zero of azimuth toward the dodecahedron is common to all of the curves for the zone $[101]$ (including the dodecahedron, Fig. 4, in the previous paper). A very broad maximum of over 180° is apparent. Experimental difficulties prohibited any reliable measurements in this sector. Probably the minimum of 0.9 at 30° is real, although the deviation from unit hardness here is of the same order of magnitude as the uncertainty of the measurements. From this curve it can be seen that a plane

FIG. 4. Zone $[\bar{1}01]$ $7\frac{1}{2}^\circ$ from octahedron.

accurately oriented in zone $[\bar{1}01]$ but otherwise differing from the dodecahedron by a small angle will produce a large error of hardness measurements with respect to those obtained on a true dodecahedron. This error chiefly occurs in azimuths from 90° to 270° .

Figure 4 represents the relative grinding hardness on a plane in zone $[\bar{1}01]$, $7\frac{1}{2}^\circ$ from the octahedron ($27\frac{3}{4}^\circ$ from dodecahedron). The direction toward the dodecahedron is most readily cut. The direction toward the octahedron is very hard. The maximum hardness seems to lie at an azimuth of 135° , although satisfactory measurements were not obtained in the sector from 100° to 260° . From this curve it can be seen that a

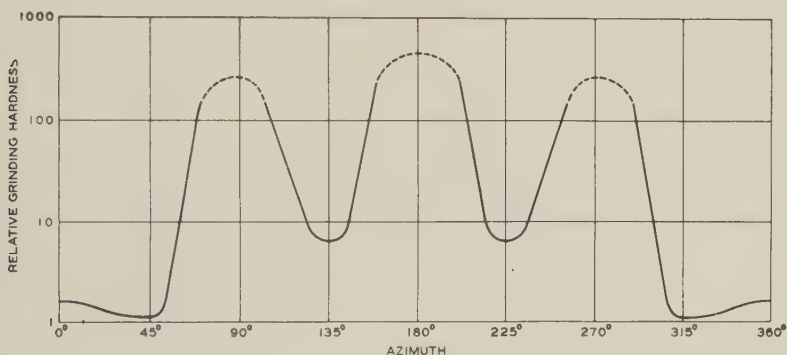


FIG. 5. Zone $[\bar{1}10]$ 15° from cube.

plane accurately oriented, located in zone $[\bar{1}01]$ but otherwise not accurately located on the octahedron, would show a hardness minimum toward the nearest dodecahedron.

In the remaining important zone, $[1\bar{1}0]$, a plane 15° from the cube was studied. The resulting curve is plotted in Fig. 5 with the zero azimuth taken as a direction toward (111) . The maximum at 0° is quite low. This is analogous to the high 45° maximum of the cube shown in Fig. 3 of the previous paper. The greatest ease of cutting in the 15° plane occurs at an azimuth of 45° . This corresponds most closely with the optimum cutting direction of the cube face. It should be noted that in Fig. 6 of the previous paper, illustrating the relative grinding hardness of a plane in zone $[1\bar{1}0]$, 39° from the cube, the zero azimuth is taken as toward the cube. Thus there is an inadvertent 180° shift of zero between these curves.

An attempt was made to obtain a curve on a plane 48° from the cube ($8\frac{3}{4}^\circ$ from the octahedron), but the results were not consistent enough to warrant plotting a curve. This plane possesses a very high grinding hardness in a direction toward the octahedron and a lower hardness toward the cube.

So far the variation of hardness along a series of azimuths for each

TABLE 1. DEPENDENCE OF GRINDING HARDNESS IN CERTAIN DIRECTIONS UPON THE ORIENTATION OF THE GRINDING PLANE

Preliminary Data

Grinding Direction		Plane Being Ground		Relative Grinding Hardness
ϕ	ρ	ϕ	ρ	
0	90	—	0	1.0 (assumed)
		90	5	1.2
		90	23	1.3
		90	38	1.0 (?)
		90	45	1.4
90	95	90	5	0.9
		0	90	1.3
270	85	90	5	x0.
		0	90	1.3
90	113	90	23	0.9
		0	90	40.
270	67	90	23	x00.
		0	90	40.
90	128	90	38	30.
		0	90	x00.
270	52	90	38	x00.
		0	90	x00.

plane has been considered. It can be seen from the data presented that for a given linear direction of grinding, the relative grinding hardness is dependent upon the orientation of the plane being ground.

As pointed out by previous investigators,³ the principal axial directions, those of a four-fold symmetry, are directions of easy grinding, while the diagonal directions, those of two-fold symmetry, are very hard directions. This is true regardless of what plane containing these directions is used for the grinding. When a crystal is ground in the [010] direction, the rela-

³ Bergheimer, H., Die Schleifhärte des Diamanten und seine Struktur: *Neues Jahrb. Min., Geol. und Pal.*, **74**, 318-332 (1938).

Kraus, E. H., and Slawson, C. B., Variations of the hardness of the diamond: *Am. Mineral.*, **24**, 661-678 (1939).

Slawson, C. B., and Cohn [sic], J. A., Maximum hardness vectors in the diamond: *Ind. Diamond Rev.*, **10**, 168-172 (1950).

Wilks, Eileen M., An interferometric investigation of the abrasion hardness properties of diamond: *Philosophical Magazine*, Ser. 7, **43**, 1140, November, 1952.

tive grinding hardness value obtained is dependent upon the position of the " $(h0l)$ " surface on which the hardness measurements are made. The dependence of the position of the ground surface along a linear direction is much more striking in more generally located linear directions. Table 1 illustrates, by way of preliminary data, this interdependence.

The linear grinding direction is expressed in ϕ and ρ values. Also the sense of the grinding is defined by these coordinates. It is assumed that the upper portion of the crystal is being ground. The plane in which the grinding direction lies is indicated by the conventional ϕ and ρ of two-circle goniometry. Thus a grinding direction of $\phi = 90$, $\rho = 95$, indicates that the grinding is toward the front of the crystal, while $\phi = 270$, $\rho = 85$, indicates that the grinding is toward the rear of the crystal. Only one direction of a kind is specified, inasmuch as the duplication of these according to the hexoctahedral symmetry would unnecessarily lengthen the table.

In grinding direction $\phi = 0$, $\rho = 90$, i.e. $[010]$, it will be noted that there is a small gradual increase in hardness as the plane is changed from (001) to (101) . The low value for the plane of $\rho = 38^\circ$ seems rather out of place. More detailed work is planned for this easy grinding direction. For a grinding direction $\phi = 90$, $\rho = 95$, the plane (010) shows a somewhat greater hardness over the $(h0l)$ plane. However, here an interpolation between 0° and 10° is involved, and the effect may not be significant. For grinding direction $\phi = 270$, $\rho = 85$, the relative grinding hardness is much greater on the " $(h0l)$ " than on (010) . Similar relations hold for the last four grinding directions in the table.

Thus it can be seen that the position of a plane being ground may profoundly affect the grinding hardness of a given grinding direction, especially in the more general directions, i.e., those that do not bear special relations to the symmetry directions of the crystal. Consequently, bond strength components in the grinding direction can not by themselves explain all of the observed variations of directional relative grinding hardness.

It will be noted that grinding hardness curves on diamond are indicative of the crystal symmetry. Surfaces accurately located normal to planes of symmetry show in the curves a line of reflection symmetry parallel to the trace of the symmetry plane. If a rotation symmetry axis is normal to the surface being ground, then a point of rotational symmetry is observed in the hardness curve. In the case of diamond, hardness measurements indicate hexoctahedral symmetry.

This investigation was carried out as a part of the Crystal Hardness program sponsored by the Office of Naval Research. The diamonds used were contributed by Industrial Distributors (1946) Ltd. of Johannesburg.

TRIMORPHISM IN ZINC SULFIDE*

DANIEL C. BUCK AND LESTER W. STROCK, *Sylvania Electric Products Inc., Bayside, Long Island, New York.*

ABSTRACT

Experimental evidence was found for the existence of a third polymorphic modification of zinc sulfide. In addition to β zinc sulfide (zincblende or sphalerite) and α zinc sulfide (wurtzite) structures, a three-layer rhombohedral structure was found to occur in the temperature range of approximately 600° C. to 1020° C. This structure is similar to the zincblende structure referred to hexagonal axes wherein the c and a dimensions are slightly altered. In conformity with conventional nomenclature it is designated γ -zinc sulfide.

The experimental evidence for the existence of rhombohedral zinc sulfide is the fine structure of cubic (111) x -ray reflections as observed with high resolution spectrometer studies on pure zinc sulfide heated for various temperatures and quenched.

The role of the rhombohedral phase in the sphalerite-to-rhombohedral-to-wurtzite transformation has been studied.

INTRODUCTION

Zinc sulfide has been known to exist in the two polymorphic forms, zincblende (β -ZnS) and wurtzite (α -ZnS), and in a series of multilayered structures.¹ Two of the latter are based on wurtzite lattice with 4- and 6-ZnS layers stacked in the [001] direction, and the other on a rhombohedral lattice, which, when referred to hexagonal axes, has 15 layers. Natural 2-layer wurtzite is the prototype of the wurtzite lattice polytypes ($4H$ and $6H$) because it is the simplest close packed hexagonal unit cell. The simplest unit cell in the rhombohedral lattice (expressed on hexagonal axes) is a 3-layer cell $3R$. A $3R$ zinc sulfide has not been previously observed. It is difficult to distinguish from face centered cubic zincblende by x -ray methods. The purpose of this paper is to present experimental evidence for the existence of a $3R$ polymorph of zinc sulfide (γ -ZnS), to describe the behavior of its lattice constants c and a (referred to hexagonal axes) in the temperature range 600° C.-1100° C., and to discuss the rôle of γ -ZnS in the transformation α -ZnS \rightleftharpoons β -ZnS.

EXPERIMENTAL

For some time the mechanism of the transformation from the zincblende to wurtzite structures has been a matter of interest, and it was in this realm of study that we obtained the experimental evidence for a 3-layered rhombohedral structure existing in the temperature range from

* Paper presented at the Toronto meeting of the Mineralogical Society of America, Nov. 11, 1953.

¹ Frondel, C., and Palache, C., *Am. Mineral.*, **35**, 29-42 (1950).

the zincblende to wurtzite transition temperature (1020°C.) down to about 600°C. In conformity with conventional nomenclature, it is designated γ -zinc sulfide. The evidence for the existence of the 3-layered rhombohedral structure was found in the fine structure of the (111) cubic reflection. Normally, zinc sulfide has a (111) cubic d -spacing of 3.12 \AA and the half width (width in angular separation at half a maximum intensity) is about $\frac{1}{3}$ degree 2θ , where θ is the Bragg angle. However,

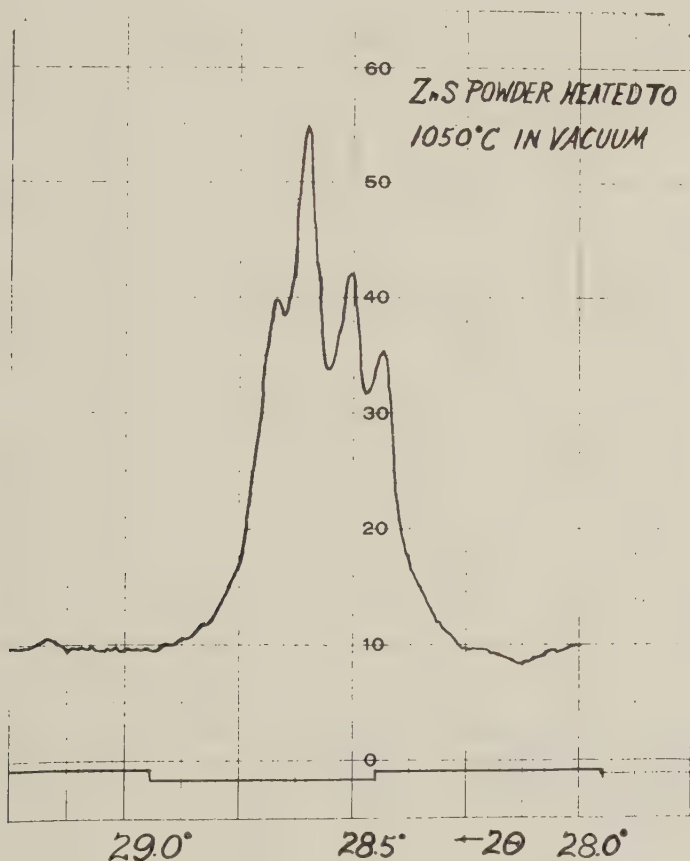


FIG. 1. Example of (111) cubic x-ray diffraction peak splitting recorded by Norelco x-ray diffraction spectrometer.

it was found that when samples of zinc sulfide powder were heated to temperatures near the transition temperature, the (111) cubic peak separated into several narrow distinct peaks with separations of the order of magnitude 0.1 degree or less. Figure 1 shows one of these split peaks,

TABLE I. RHOMBOHEDRAL PHASE IN HEAT TREATED CUBIC ZNS POWDER
 (Annealed samples first heated to 1050° C. and quenched)

Temperature °C.	Split cubic (111) spacings in Å (Hexagonal indices)		Rhombohedral cell in Å			From (100) spacing of hexagonal phase present <i>a</i>
			Hexagonal axes		Ratio <i>c/a</i>	
	101	003	<i>a</i>	<i>c</i>		
950	3.113	3.121	3.811	9.363	2.457	3.818
1000	3.131	3.143	3.833	9.429	2.460	3.816
1050	3.122	3.136	3.822	9.408	2.462	3.824
Annealed at						
1000	3.131	3.159	3.830	9.477	2.474	3.822
950	3.113	3.122	3.811	9.366	2.457	3.810
900	3.127	3.135	3.829	9.405	2.456	3.808
850	3.112	3.116	3.811	9.348	2.453	3.805
Cubic	(111) 3.121		3.822	[111] 9.363	(2.4495)	geometrical ratio

as recorded by a high-resolution *x*-ray diffraction spectrometer.

Samples of zinc sulfide powder were sealed in evacuated quartz vials and heated to the temperatures indicated in Column 1 of Table I, and quenched in water at room temperature. Also powder which had been heated to 1050° C. for 2½ hours and quenched, was then annealed at temperatures between 1000° C. and 850° C.

In these annealed samples, the (111) cubic peak splitting remains until the temperature is lower than 850° C. The angular separation of the components of the multi-peaked reflections varied appreciably over the temperature range 850-1050° C., the spread being greater at higher temperature. The relative intensity of the minor peak components is greater at higher temperature.

Figure 2 shows the (111) planes of the zincblende structure referred to a hexagonal axis system whose base (001) plane is the (111) plane of the original face centered cubic cell and the *c* axis of this 3-layered hexagonally based cell is the body-diagonal of the face centered cube. To investigate the effects of temperature on the form of the *x*-ray diffraction reflections, we will consider two simple models. If the crystal undergoes isotropic thermal expansion, the spacings of all planes in the crystal will increase uniformly. If the rates of thermal expansion vary over a small range according to some parameter, such as position in the crystal, the diffraction line will be broadened as well as moved towards lower Bragg

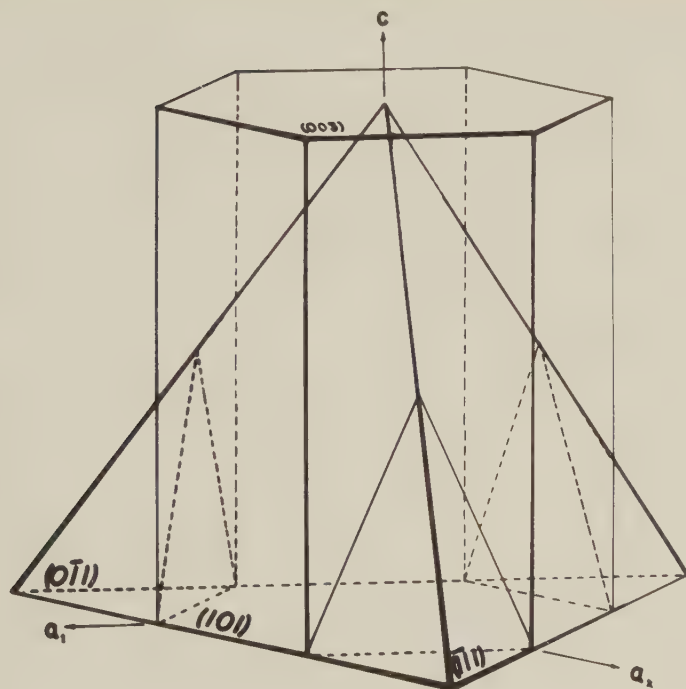


FIG. 2. (111) cubic planes referred to a 3-layer hexagonal axis system and indexed in the hexagonal system.

angles. However, if the crystal enlarges in a preferred direction, a reduction of symmetry will occur, causing degenerate reflections to be separated into component reflections whose interplanar spacings have different expansion coefficients. Such a case is the system of (111) cubic planes in face centered zinc sulfide. Referring to Fig. 2, if the enlargement is greater in the [003] direction than in the other three ([101], $[\bar{1}11]$, $[0\bar{1}1]$), the interplanar spacing of the (003) planes will increase faster than those of the (101), $(\bar{1}11)$, $(0\bar{1}1)$ planes thus producing two distinct interplanar spacings where there was formerly one for all (111) cubic planes. This transformation can be described by an elongation of a cube along its body diagonal. When the structure is cubic, the angle between the shortest rhombohedral axes is 60° . When the figure undergoes the elongation, these angles decrease from 60° .

Table I shows that at temperatures above 850°C . the (111) cubic line resolves itself into 3 peaks and at temperatures above 1000°C ., becomes 4 peaks; also, the (100) hexagonal line is resolved into 2 peaks in this temperature range. This indicates the concurrent existence of both nor-

mal (room temperature) cubic zinc sulfide and a structure which, when referred to the hexagonal system, has a $c:a$ ratio greater than 2.4495 (that of a perfect face centered cube), where the a value is slightly smaller than that of natural zinc sulfide and the c axis is larger. This latter structure is, therefore, rhombohedral whose interaxial angle is slightly less than 60° .

The third split (111) "cubic peak" mentioned above corresponded to some undistorted cubic zinc sulfide which either reverted to its original form within the quenching time allowed, or never had time to make the transformation to rhombohedral. The other two (111) "cubic peaks" corresponded to the reflections from the $(\bar{1}11) + (0\bar{1}1) + (101)$ and the (003) $3R$ planes (Fig. 2). The (003) $3R$ plane corresponds with the smaller Bragg angle peak. Since the planes (003) cut only the c axis of the $3R$ cell, the length of the c axis is simply equal to three times the spacing of this reflection. Then, since the (101) type planes all cut both the c and a axes of the $3R$ cell (referred to hexagonal axes), it was possible to compute the length of the a axis using the value of the c axis obtained above from the (003) spacing. This a axis value could not be compared with one determined directly from (100) spacings, since this is an extinction in a 3-layer structure (rhombohedral or cubic on hexagonal axes) but it was compared with the a axis spacing determined from (100) reflections of hexagonal (2H) structure present in the same powder samples. The a axis values for the hexagonal phase were all lower than those for the rhombohedral phase; meaning that the rhombohedral to hexagonal phase is accompanied by further shrinkage of the a axis. All of these changes, except the 950° C. annealed sample, are greater than the experimental peak splitting resolution of 0.002 \AA . The c/a ratio for the rhombohedral phase increases with temperature above the equivalent cubic value 2.4955 as shown in Table I.

It was not known whether the cubic to rhombohedral transition was a phenomenon occurring within the powder particles or a phenomenon associated with recrystallization from the vapor phase. To investigate this the apparatus in Fig. 3 was built. The system was pumped to a vacuum of about 10^{-1} mm. Hg. This reduced the chance of ZnO formation and the effect of impurities acting in the recrystallization process. The zinc sulfide is heated in boat #1 to $1050\text{--}1100^\circ$ C. and recrystallization, if any, occurs on boat #2 due to its lower temperature. Since the vapor pressure of zinc sulfide climbs rapidly above 1000° C., it was not surprising that much recrystallized zinc sulfide was found in boat #2. The powder left in boat #1 was examined under the microscope and in several cases recrystallized zinc sulfide was noticed. Figure 4 shows the interplanar spacings calculated from the (111) cubic diffraction component peaks for recrystallized zinc sulfide for four experiments varying the tem-

perature of the boat upon which the crystals formed. Again, the angular spread between peaks is an increasing function of temperature. The largest peak remained in the d (111) cubic position, and as temperature rose, peaks spread out in both larger and smaller d -spacing directions.

The most probable mechanism to explain Fig. 4 is a superposition of untransformed cubic (111) reflections and reflections from $3R$ cells where again the a axes shrink and the c axis enlarges, resulting in spacings less

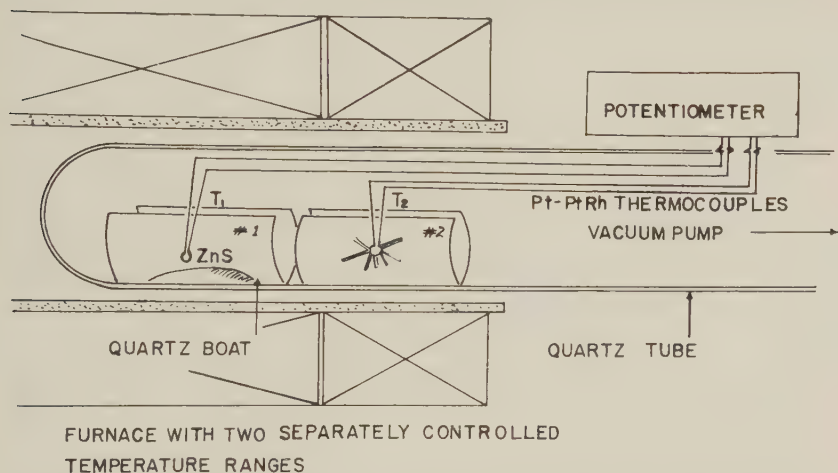


FIG. 3. Crystal growing furnace and vacuum system. ZnS powder is introduced in boat #1 and heated to temperature T_1 . The vacuum is maintained until the powder has attained the temperature T_1 . The pump is then shut off and the vapor pressure of ZnS at T_1 determines the pressure of the system. To quench, the furnace is slid off to left.

and greater than the regular (111) cubic spacing. At 600°C . the cubic reflection and the slower increasing (101) ($3R$) reflections practically coincide; at higher temperatures the (101) $3R$ spacing reflection decreases and in the 1000°C .– 1100°C . sample these spacings differ by 0.10 \AA , about 6 times the corresponding difference at 900°C . Thus, we see an elongation of the cell along the c axis and a corresponding compression of the hexagonal base varying continuously with the temperature. X-ray rotation photographs of single crystals grown at these elevated temperatures revealed an amount of hexagonal zinc sulfide, whose (002) reflection from our 1100°C . sample is the one with the next to largest spacing. The transformation resulting in this $2H$ cell is best described in several steps:

A differential thermal expansion occurs in one preferred of the four (111) cubic directions where zinc and sulfur ions are lined up. This direction we will call [003] in the 3-layered hexagonal structure. The sulfur presumably becomes asymmetric and orients its long axis in this pre-

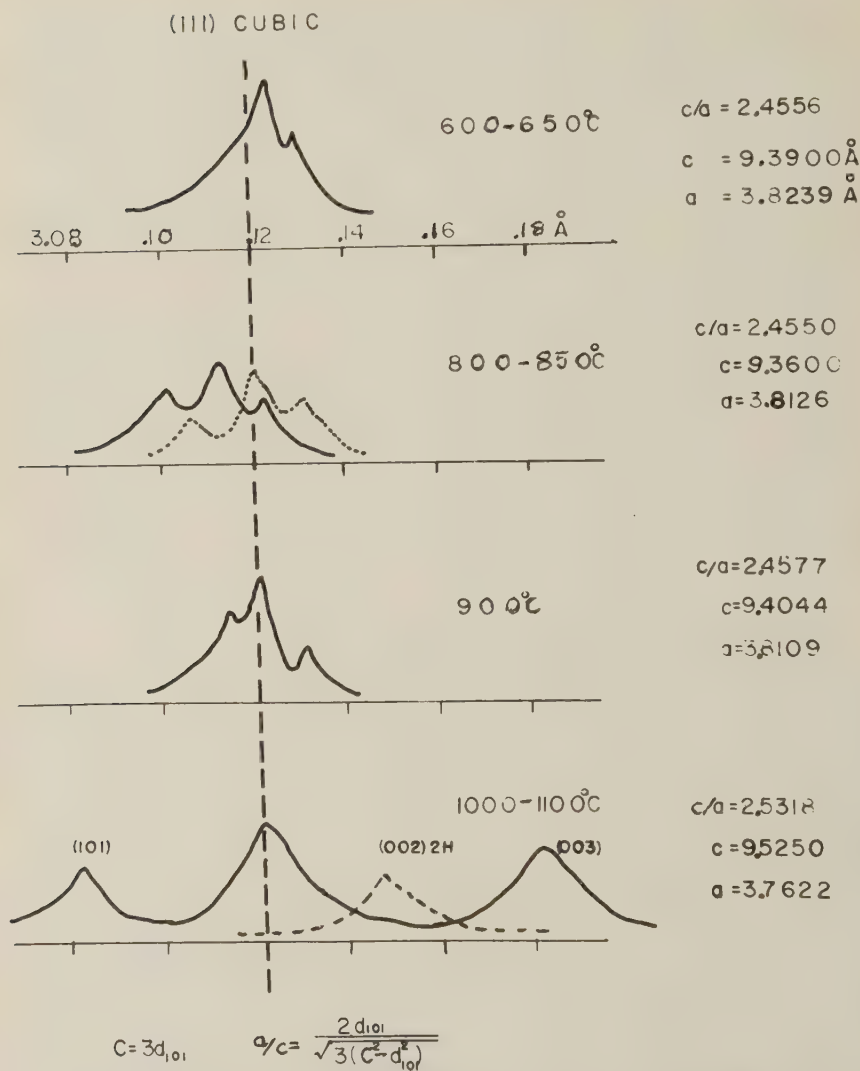


FIG. 4. Positions of (111) cubic x-ray diffraction peaks for ZnS crystals grown from the vapor phase at different temperatures of crystal growth. The dotted curve at 800-850°C. indicates correction for an unusually long quenching time. Curves obtained from powder plaque sample.

ferred [003] direction. As the expansion increases, there is a corresponding decrease in the influence of an (003) layer on the atoms settling down from the vapor phase into the second layer above the original. This causes an increasing probability of second layer atoms to land on an *AB* pair of

layers forming an *ABAB* (*2H*) sequence rather than an *ABC* (*3R*) sequence. At the conventionally accepted zincblende-wurtzite transition temperature (1020° C.) this probability is theoretically unity. The *2H* cells which result from a vapor to solid phase transformation have *c* axes longer than that found in natural wurtzite; this is so because these crystals were quenched relatively quickly with respect to those in nature, and most of the *2H* cells are found in crystals which also have *3R* cells in them, indicating that these crystals are still strained because they were grown at a high temperature. However, some pure *2H* crystals were found from a vapor phase deposition at 1100° C. showing that the *3R*→*2H* transition probability can be unity at a sufficiently high temperature.

The mechanism proposed above is corroborated by the study of a rotation x-ray diffraction photograph of a single crystal grown between 800° C. and 850° C. The portion of the crystal that was examined was a flat thin striated plane, and the axis of rotation was perpendicular to the striations and in the plane of the crystal. The spacings for the (003) and (101) planes in the face centered cubic, all referred to hexagonal axes, were accurately measured and found to be unequal. The spacings were:

$$d_{(003)} = 3.1399 \text{ \AA}, \quad d_{(101)} = 3.1200 \text{ \AA}.$$

The length of the *c*-axis of this cell is 3 times the (003) spacing = 9.4197 Å, and the *c/a* ratio calculated from the formula

$$\frac{c}{a} = \frac{\sqrt{3}}{2} \frac{\sqrt{C^2 - d_{(101)}^2}}{d_{(101)}} = 2.467,$$

and the *a*-axis was found to be 3.8183 Å. The cell thus described was in general agreement with the cell described by the spectrometer measurements on the 800–850° C. crystal sample. Also, if rhombohedral zinc sulfide is a high temperature form, it would be expected to be metastable at room temperature to such treatments as cold working. This was found to be so; after several minutes working with the mortar and pestle, the diffraction peak splitting was completely removed from a sample of *3R* powder.

Comparison of Fig. 4 and Table I reveal an inconsistency in *c/a* axial ratio values at given temperatures for the heated powder samples and the crystals grown from the vapor phase. This is due to the difference in quenching times of the two types of experimental samples. The powders took about a minute to cool down to room temperature, whereas the crystals required only a few seconds to cool as they were grown on a Pt-PtRh thermocouple which cooled off quickly. The crystals then had less time to revert to lower temperature forms and they gave a more accurate picture of the structures existing at the elevated temperatures.

In case of the samples of zinc sulfide powder, heated to elevated

temperatures, the vapor was continually swept away by the vacuum pump. However, some recrystallization was discovered in these samples, making it to date impossible to decide whether or not the γ - α zinc sulfide transformation occurs within the volume of the powder particles.

CONCLUSIONS

There exists a third polymorphic modification of ZnS which acts as an intermediate phase between the isometric cubic structure and the directional wurtzite structure. As the temperature increases, the inter-atomic forces become more directional and the symmetry of the structure reduces from the fourfold cubic to the threefold rhombohedral, and finally to the threefold hexagonal wurtzite. γ ZnS has been found at temperatures from 1020° C. down to 600° C. It is reasonable to expect that crystals will be found with rhombohedral structures of $c:a$ ratios ranging from the equivalent cubic value 2.4495 up to a maximum value at the rhombohedral-hexagonal transition temperature.

Manuscript received Jan. 11, 1954.

RABBITTITE, A NEW URANYL CARBONATE FROM UTAH*

MARY E. THOMPSON, ALICE D. WEEKS, AND ALEXANDER M. SHERWOOD,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

Rabbittite is a new hydrated calcium magnesium uranyl carbonate found in the Lucky Strike No. 2 mine, San Rafael district, Emery County, Utah, in July 1952. It is pale green, finely acicular to fibrous, silky, and occurs as an efflorescence on the mine wall. It is optically biaxial, probably positive, with indices of refraction $\alpha = 1.502 \pm 0.005$, $\beta = 1.508 \pm 0.005$ and $\gamma = 1.525 \pm 0.003$. The specific gravity is about 2.6. The chemical analysis shows CaO 10.6 per cent, MgO 9.2, UO_3 37.4, CO_2 17.8, H_2O 24.5, acid insoluble 0.5; total 100 per cent, and indicates the formula $\text{Ca}_3\text{Mg}_3(\text{UO}_2)_2(\text{CO}_3)_6(\text{OH})_4 \cdot 18\text{H}_2\text{O}$. An x -ray rotation photograph of a small bundle of fibers shows the unit cell length $c_0 = 9.45 \pm 0.05 \text{ \AA}$. From the indexing of $hk0$ reflections a_0 is thought to be $32.6 \pm 0.1 \text{ \AA}$ and b_0 $23.8 \pm 0.1 \text{ \AA}$, with $Z = 8$.

INTRODUCTION AND ACKNOWLEDGMENTS

Rabbittite was collected from the Lucky Strike No. 2 mine, Emery County, Utah, in July 1952 by M. E. Thompson and A. D. Weeks when they visited the mine with other U. S. Geological Survey geologists. The mineral was determined as a new one because its x -ray diffraction powder pattern and its physical and optical properties differ from those of other known uranium carbonates.

Of the uranyl carbonates in the literature, only swartzite might be confused with rabbittite. Swartzite is, however, definitely distinct from rabbittite, and to make the differences clear the optical properties, chemical analysis, and d -spacings of the x -ray powder pattern of swartzite are included for comparison with those of rabbittite.

Rabbittite is named in honor of John C. Rabbitt, who was chief of the U. S. Geological Survey Trace Elements Section from 1947 to 1953—in recognition of the leadership and inspiration he gave to the members of the laboratory.

Thanks are gratefully extended to J. W. Gruner, University of Minnesota, for loan of an ore sample from the Lucky Strike No. 2 mine.

This work was part of a project on mineralogy of uranium in sandstone-type deposits that is being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

OCCURRENCE

Rabbittite occurs as an efflorescence on a pillar of high-grade ore near the portal of the Lucky Strike No. 2 mine, Emery County, Utah. The

* Publication authorized by the Director, U. S. Geological Survey.

mine is in a uranium deposit in the Shinarump conglomerate (Triassic), between the San Rafael River and the Muddy River on the west flank of the San Rafael Swell. Figure 1 is an index map showing the location of the mine. The ore contains pitchblende and is only partly oxidized because the deposit is protected by the overlying Chinle formation and Wingate sandstone, which rise in a high cliff above the mine. The ore near the portal was high grade, containing pitchblende with a little

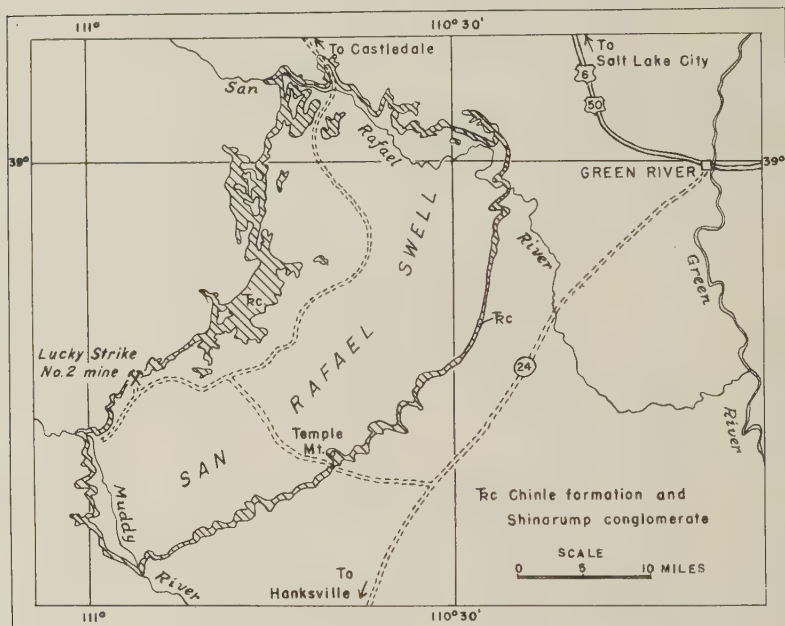


FIG. 1. Index map of locality of rabbitite.

pyrite and galena, and many yellow and orange secondary uranium minerals, including fourmarierite,¹ rabbitite, zippeite, another uranium sulfate that is related to zippeite, and another new uranium mineral, possibly magnesium uranyl sulfate, whose description is not yet completed. Gypsum and at least two pink cobalt efflorescences, Bieberite and sphaerocobaltite, were collected from the same pillar on which the rabbitite occurred.

PHYSICAL AND OPTICAL PROPERTIES

Rabbitite occurs as bundles of pale-green extremely small acicular crystals with a silky luster. The bundles of fibers resemble talc, in that some of them are bent and twisted.

¹ Specimen courtesy of J. W. Gruner.

The hardness of rabbittite was determined approximately by rubbing it against gypsum and calcite while viewing the test through the binocular microscope. The mineral seems to be slightly harder than gypsum. If it is crushed too roughly when being prepared as a spindle for an x-ray powder photograph, the resulting picture shows broadened reflections. The mineral effervesces in dilute HCl and is slowly soluble in cold water. The specific gravity was measured by suspending grains of the mineral in a mixture of bromoform and acetone. The mineral floats just under the surface of a liquid with specific gravity of 2.57.

Rabbittite is considered to be monoclinic on the basis of its optical properties. The small acicular crystals are elongated parallel to the *c*-axis. Under the microscope the crystals show a cleavage across the fibers, which is probably parallel to {001}, and two easy and perfect prismatic cleavages.

Even with the aid of an oil-immersion lens, individual crystals of rabbittite are too small to give an interference figure. The fibers in some of the bundles seem to lie in parallel orientation, and measurements of the optical constants were made on several such bundles. Some of the bundles seem to be flattened on {100} and give an optical figure thought to be an obtuse bisectrix figure.

The optical properties of rabbittite are distinctly different from those of swartzite, as shown below:

Orientation	<i>Rabbittite</i>	<i>Swartzite</i>
	<i>n</i>	<i>n</i>
X	1.502 ± 0.005	1.465
Y = <i>b</i>	1.508 ± 0.005	1.51
Z \wedge <i>c</i> $\sim 15^\circ$	1.525 ± 0.003	1.540
	Biaxial positive (?)	Biaxial negative

CHEMICAL COMPOSITION

With the aid of a binocular microscope, slightly less than 0.1 g. of rabbittite was handpicked for analysis. The mineral was concentrated by picking the largest aggregates of rabbittite from the friable sandstone. The aggregates were crushed, examined under the binocular, and further purified. A semiquantitative spectrographic analysis made by C. S. Annell on a 10-mg. sample showed more than 10 per cent U, 1 to 10 per cent Mg and Ca, 0.1 to 1 per cent Si, and 0.01 to 0.1 Al and Y. About 75 mg. was available for the chemical analysis (Table 1) made by A. M. Sherwood.

In the chemical analysis of rabbittite the sample was first dissolved in

TABLE 1. CHEMICAL ANALYSIS AND THEORETICAL COMPOSITION OF RABBITTITE AND CHEMICAL ANALYSIS OF SWARTZITE

	Rabbittite		Swartzite
	Analysis of 75 mg. by A. M. Sherwood	$\text{Ca}_3\text{Mg}_3(\text{UO}_2)_2(\text{CO}_3)_6$ (OH) $_4 \cdot 18\text{H}_2\text{O}$	Analysis in Axelrod <i>et al.</i> (1951) by F. S. Grimaldi
CaO	10.6	11.32	7.32
MgO	9.2	8.09	5.47
UO ₃	37.4	38.54	38.85
CO ₂	17.8	17.79	17.92
H ₂ O	24.5	24.26	29.69
Acid insoluble	0.5		0.75 (rem.)
Total	100.0	100.00	100.00

water, and carbon dioxide was determined by titration with standard HCl. The silica was removed by volatilization with HF. The uranium was then separated with NH_4OH , reduced, and titrated with $\text{K}_2\text{Cr}_2\text{O}_7$. Calcium was precipitated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and ignited to CaO; and the magnesium was precipitated with $(\text{NH}_4)_2\text{HPO}_4$ and ignited to $\text{Mg}_2\text{P}_2\text{O}_7$. Total loss on ignition at 900°C . was determined, and the per cent CO_2 was subtracted from it to calculate the total H_2O .

The analysis indicates that the formula is probably $\text{Ca}_3\text{Mg}_3(\text{UO}_2)_2(\text{CO}_3)_6(\text{OH})_4 \cdot 18\text{H}_2\text{O}$ and that it differs from that of the other magnesium and calcium uranyl carbonates—bayleyite $\text{Mg}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 18\text{H}_2\text{O}$, swartzite $\text{CaMg}(\text{UO}_2)(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ (Axelrod *et al.*, 1951), and liebigitte $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 9\text{H}_2\text{O}$ (?). Swartzite contains the same elements as rabbittite but in different proportions. The chemical analysis of swartzite in given in Table 1.

X-RAY DIFFRACTION DATA

The x-ray powder pattern of rabbittite distinguishes it from the other uranyl carbonates although, in common with the others, its powder pattern contains a number of lines with large d -spacings, indicating a large unit cell. The pattern obtained with the x-ray spectrometer shows the closely spaced inner lines (Table 2) with much better resolution than the ordinary powder pattern. The d -spacings of swartzite, as given in Axelrod *et al.* (1951), are listed in Table 2 with those of rabbittite. From an x-ray rotation photograph of a bundle of fibers of rabbittite around the c -axis, c_0 was found to be $9.45 \pm 0.05 \text{ \AA}$ (personal communication, H. T. Evans, 1953). The zero-layer reflections were indexed graphically, using a modi-

TABLE 2. X-RAY DIFFRACTION POWDER PATTERNS OF RABBITTITE AND SWARTZITE
 (d -spacings of rabbitite measured on x -ray spectrometer pattern,
 $1/4^\circ$ per minute, Cu/Ni radiation)

Rabbitite		Swartzite ¹	
I	d	I	d
3	19.4	10	8.76
1	18.6	9	7.31
5	11.28	5	6.37
3	8.63	1	5.83
10	8.24	10	5.50
8	7.79	1	5.13
3	7.15	8	4.82
1	6.81	2	4.62
3	6.47	2	4.46
1	6.35	2	4.37
5, broad	5.83	2	3.85
5	5.72	7	3.66
3	5.22	5	3.53
5	4.81	1	3.39
7	4.71	1	3.31
1	4.51	1	3.25
8	4.37	7	3.19
1	4.28	2	3.11
3	4.05	1	3.04
3	4.03	8	2.91
3	3.84	2	2.82
1, broad	3.71	5	2.61
3	3.60	4	2.28
5	3.33	3	2.23
		2	2.19
		2	2.10
		8	2.06
		5	1.817
		8	1.707
		2	1.375
		2	1.268
		3	1.217
		2	0.9615

¹ Axelrod *et al.* (1951).

fied version of Bjurström's chart (Bunn, 1946, p. 280) and the $hk0$ indices thus obtained are listed in Table 3. The a and b axes appear to be at right angles to one another, and according to the graphical solution $a_0 = 32.6 \pm 0.1 \text{ \AA}$ and $b_0 = 23.8 \pm 0.1 \text{ \AA}$. The number of formula units in the unit cell, is probably 8; by calculation from the approximate figures for

TABLE 3.—TENTATIVE INDEXING OF $hk0$ REFLECTIONS OF RABBITTITE
(X-ray rotation photograph around c -axis; Cr/V radiation;
 $a_0=32.62$, $b_0=23.77$)

	$a_0=32.62$	$b_0=23.77$	
I	d (meas.)	d (calc.)	$hk0$
5	19.0	19.21	110
3	16.2	16.3	200
4	13.5	13.45	210
3, broad	12.0	11.88	020
7	11.24	11.17	120
3	9.89	9.89	310
3	9.60	9.60	220
3	8.96	—	—
10	8.13	8.15	400
		8.02	320
		7.92	030
3	7.71	7.71	410
		7.70	130
3	7.13	7.13	230
1	5.95	5.94	040
3	5.82	5.85	140
3	5.70	5.72	520
		5.68	430
1	5.21	5.21	340
5	4.80	4.80	440
		4.75	050
5	4.70	4.71	150
5	4.40	4.39	540
5	4.34	4.36	350
1	4.10	4.11	450
3	4.03	4.01	640
5	3.84	3.85	260
		3.84	550

a_0 , b_0 , c_0 , from the specific gravity, and with no allowance made for β angle differing from 90° , the number of formula units is 7.8. The mineral is considered monoclinic because of its optical properties. The β angle cannot be accurately determined on the present material, but it is probably close to 90° .

REFERENCES

- AXELROD, J. M., GRIMALDI, F. S., MILTON, C., AND MURATA, K. J. (1951), The uranium minerals from the Hillside mine, Yavapai County, Arizona: *Am. Mineral.*, **36**, 1–22.
BUNN, C. W. (1946), *Chemical Crystallography*, London, Oxford Press, 422 p.

Manuscript received April 1, 1954.

NAVAJOITE, A NEW VANADIUM OXIDE FROM ARIZONA*

ALICE D. WEEKS, MARY E. THOMPSON, AND ALEXANDER M. SHERWOOD,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

Navajoite, hydrated vanadium pentoxide, is a new mineral found in the Monument No. 2 mine on the Navajo Indian Reservation, Apache County, Ariz. It occurs as a coating around pebbles and sand grains and as thin seams in sandstone and clay lenses in a vanadium-uranium deposit in the Shinarump conglomerate (Triassic). It is dark brown, soft, and fibrous, with silky luster and brown streak. The specific gravity, measured on the Berman balance, is 2.56. The mineral is optically biaxial, probably negative, has parallel extinction, and $\alpha = 1.905 \pm 0.003$, β about 2.02, and γ slightly above 2.02. X is yellowish brown, Y is yellowish brown, and Z is dark brown parallel to fiber length. A chemical analysis shows V_2O_5 71.68 per cent, V_2O_4 3.08, Fe_2O_3 3.58, H_2O 20.30, SiO_2 1.20, and CaO 0.22; total 100.06 per cent, and indicates the formula $V_2O_5 \cdot 3H_2O$. The d -spacings and intensities of lines in the x-ray powder pattern are listed. The unit cell length along the fiber is 3.65 ± 0.03 Å. Tentative indexing of the powder pattern suggests that the mineral is monoclinic with $a_0 = 17.43 \pm 0.10$ Å, $b_0 = 3.65 \pm 0.03$ Å, $c_0 = 12.25 \pm 0.10$ Å, $\beta = 97^\circ \pm 30'$, and $Z = 6$.

INTRODUCTION AND ACKNOWLEDGMENTS

Several impure samples of navajoite were collected from the Monument No. 2 mine in the Garnet Ridge quadrangle, Apache County, Ariz., in 1951. The first seen by the writers was collected by A. Rosenzweig, at that time mineralogist for the Atomic Energy Commission in Grand Junction, Colo. In July 1951 A. D. Weeks, D. H. Johnson, and other U. S. Geological Survey mineralogists collected several samples. Clifford Frondel of Harvard University sent the writers a sample that had been submitted to him. All of these samples were sandstone or shaly sandstone impregnated with the brown vanadium mineral, but they contained too small a concentration of pure mineral for chemical analysis. In July 1952 A. D. Weeks and M. E. Thompson visited the mine again with Survey geologists and found enough relatively pure material to establish the new mineral.

When the chemical composition was found to be hydrated vanadium pentoxide, an effort was made to compare this mineral with alaite reported from Russia as a hydrated vanadium oxide (Nedadkovich, 1909). No alaite specimen has been located, and the original description gives no chemical analysis or adequate description of physical properties. It has been suggested that alaite may be hewettite or metahewettite (Hillebrand, Merwin, and Wright, 1914, p. 49; and Fersman, 1930, p. 33), probably because of its red color. Therefore it seemed unwise to use the

* Publication authorized by the Director, U. S. Geological Survey.

uncertain name alaite for the new Arizona material, and the name navajoite has been chosen in honor of the Navajo Indians on whose reservation this new mineral occurs.

Thanks are gratefully extended to A. Rosenzweig and Clifford Frondel for an opportunity to examine their samples, to H. T. Evans for x-ray data, and to W. T. Schaller and D. H. Johnson for helpful suggestions.

This investigation is part of the project of mineralogic studies on the Colorado Plateaus being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

OCCURRENCE

All samples collected by the writers came from the South Rim workings of the Monument No. 2 mine, operated by the Vanadium Corporation of America. (It is not known whether Frondel's and Rosenzweig's samples came from the same part of the mine.) The mine is in a vanadium-uranium deposit located just north of Comb Ridge in Monument Valley. The ore occurs in a wide, complex channel that is filled with Shinarump conglomerate (Triassic) and that extends down through the Moenkopi formation (Triassic) into the DeChelly sandstone member of the Cutler formation (Permian) (Witkind et al., 1953).

The mineral navajoite impregnates conglomeratic sandstone and silty sandstone, forms seams in the sandstone and crescent-shaped coatings above and below pebbles, and fills small fractures in clay lenses. The best specimens are the thickest crescent-shaped coatings and seam fillings with fibers perpendicular to the wall rock. The wall rock is porous and friable, and most of the ore in this part of the mine is highly oxidized. Associated minerals include only one with V^{+4} and V^{+5} , corvusite, and the rest are fully oxidized: tyuyamunite, rauvite, hewettite, steigerite, and limonite.

PHYSICAL PROPERTIES

Navajoite is dark brown, silky to fibrous, with brown streak, and adamantine luster on freshly broken surfaces. The fibrous appearance is due to the growth habit, as minute columns build up perpendicular to a fracture surface. The fibers are very soft, and when finely ground on a glass slide they smear out to form a waxy yellow-brown film. Some corvusite has a similar growth habit, but it may be distinguished by its blue-black color and especially by its greenish color when smeared thin on a glass slide. The hardness of navajoite is less than 2; and the specific gravity, measured on a Berman balance, is 2.56. The mineral is so dark and fine grained that the optical properties have not been completely

determined. It is biaxial, probably negative, has parallel extinction, and $\alpha = 1.905 \pm 0.003$, β approximately 2.02 and γ is slightly above 2.02. X is yellowish brown, Y is yellowish brown, and Z is dark brown parallel to the fiber length. Although optically the mineral appears to be orthorhombic, x-ray study indicates that it may be monoclinic and elongated parallel to the b axis, as hewettite was proved to be by Barnes and Qurashi (1952).

CHEMICAL ANALYSES

The samples collected in 1951 contained quartz, clay, and other contaminants and were not suitable for a chemical analysis to determine the composition of a new mineral. In one of the samples collected in 1952 a crescent-shaped mass of navajoite around a quartzite pebble about $1\frac{1}{2}$ inches in diameter seemed very pure. About 1 g. of this was prepared for chemical analysis, and a portion of the original specimen was saved to show the occurrence. The outer and inner surfaces of the crescent were scraped to remove any hewettite or rauvite that coated them, then the navajoite was ground and examined under the binocular microscope for impurities. A semiquantitative spectrographic analysis made by H. W. Worthing on 10 mg. of the purified sample is as follows:

Over 10 per cent	V
1-10	Fe
0.1 - 1.0	Si, Ca, Al
0.01 - 0.1	Ba, Na, Mg
0.001- 0.01	Cr, Ti, Sr, Y, Mn, Cu

Because the analysis shows the constituent elements of the contaminating quartz and clay to be each less than 1 per cent, this sample was the most suitable one available for chemical analysis.

The interpretation of the chemical analysis is chiefly concerned with

TABLE 1. CHEMICAL ANALYSIS OF NAVAJOITE
A. M. Sherwood, *analyst*

	Per Cent
V ₂ O ₅	71.68
V ₂ O ₄	3.08
Fe ₂ O ₃	3.58
SiO ₂	1.20
CaO	0.22
H ₂ O	20.30
Total	100.06

the water content and with the question of impurities in the sample, or the solid solution substitution of some minor constituents. The 1.20 per cent of silica is probably due to quartz impurity. The 0.22 per cent of CaO may represent contamination by about 3 per cent of hewettite, although no lines of hewettite show in the x -ray powder pattern of navajoite. The presence of a small amount of hewettite would not affect the calculation of the formula for navajoite because the proportion of V_2O_5 to H_2O is thought to be the same in both minerals. No lines in the x -ray pattern of navajoite indicate that the 3.58 per cent of Fe_2O_3 is present as an impurity of goethite or of fervanite ($Fe_4V_4O_{16} \cdot 5H_2O$). Probably the iron substitutes for vanadium in this mineral as it does in montroseite (Weeks, Cisney, and Sherwood, 1953; and Evans and Block, 1953). If the 3.08 per cent of V_2O_4 is present in admixed corvusite and if its formula is $V_2O_4 \cdot 6V_2O_5 \cdot 13H_2O$, corvusite would make up nearly 28 per cent of the analyzed sample. Such a high contamination is unlikely for the following reasons: (1) navajoite is dark brown and the streak brown instead of black and greenish black as in corvusite; (2) the x -ray powder pattern of navajoite has been indexed (Table 3) with reasonably satisfactory results and does not seem to be a mixed pattern; (3) the presence of corvusite is probably not indicated in the pattern of navajoite, although the two minerals may have some structural features in common. The pattern of corvusite is not very well established and seems to be somewhat variable. It is believed that navajoite formed by oxidation of corvusite at the Monument No. 2 mine and that the conversion to navajoite structure took place in this sample before the oxidation was completed.

A redetermination of the water as H_2O- and H_2O+ made nearly a year after the original chemical analysis shows 10.21 per cent of H_2O- and 8.10 per cent of H_2O+ . This represents a loss of 1.99 per cent of water while the sample was stored in the laboratory and indicates that part of the water is easily released, perhaps as interlayer water. The 8.10 per cent of H_2O+ indicates that one molecule of water is held in the structure. Although the molecular proportion of water to V_2O_5 in the chemical analysis is slightly less than 3, the formula is probably $V_2O_5 \cdot 3H_2O$ with two molecules of interlayer water and one structural. If more pure material can be obtained, dehydration studies will be made.

X-RAY DIFFRACTION DATA

The x -ray powder pattern (Table 2) of navajoite distinguishes it readily from hewettite and corvusite, which it resembles in physical appearance. The best fibrous sample (same as that chemically analyzed) gives an oriented x -ray pattern. The fibers are too small for single crystal x -ray

TABLE 2. X-RAY DIFFRACTION POWDER PATTERN OF NAVAJOITE
(AVERAGE OF 5 PATTERNS)

CuK α radiation

d (meas.) Å	I	d (meas.) Å	I
12.11	VS	3.10	Wb
10.61	M	2.90	M
9.41	F	2.79	F
8.67	F	2.68	F
7.44	F	2.49	W
5.79	Wb	2.39	VF
4.35	W	2.18	F
3.95	F	2.12	M
3.53	W	1.99	W
3.47	W	1.80	F

photographs. However, a rotation photograph (taken by H. T. Evans, U. S. Geological Survey) of a small bundle of fibers indicates that the unit cell length along the fiber is about 3.65 Å. A large-scale photograph of the zero layer was then obtained by placing the fiber bundle in a powder camera and using chromium radiation. An attempt to index the zero layer by use of the logarithmic form of Bjurström's chart (Bunn, 1946, p. 380) failed, indicating that the two axes other than the fiber length are not at right angles to each other and navajoite is probably monoclinic.

The reciprocal lattice spacings ($1/d$) of the ($h0l$) lines with spacing larger than $1/d_{010}$ were plotted. The best graphical solution found by

TABLE 3. TENTATIVE INDEXING OF $h0l$ LINES OF NAVAJOITE POWDER PATTERN

Cr/V radiation

I	d (meas.) Å	d (calc.) Å	hkl	Assume:
W	17.4	17.33	(100)	$a_0 = 17.43$ Å
VS	12.1	12.15	(001)	$b_0 = 3.65$ Å
M	10.6	10.58	(101)	$c_0 = 12.25$ Å
VF	9.4	9.42	(10 $\bar{1}$)	$\beta = 97^\circ$
F	8.66	8.65	(200)	$V_2O_5 \cdot 3H_2O$
Fb	7.41	7.496	(201)	$Z = 6$
Wb	5.79	5.767	(300)	
F	4.32	4.325	(400)	
F	3.95	3.951	(302)	

trial and error suggests that $a_0 = 17.43 \pm 0.10$ Å, $b_0 = 3.65 \pm 0.03$ Å, $c_0 = 12.25 \pm 0.10$ Å, and $\beta = 97^\circ \pm 30'$. This unit cell would hold approximately 6 formula weights of $V_2O_5 \cdot 3H_2O$. The tentative indexing of the larger d -spacings is given in Table 3. It is hoped that larger crystals will be found so that the crystallography may be checked.

REFERENCES

- BARNES, W. H., AND QURASHI, M. M. (1952), Unit cell and space group data for certain vanadium minerals: *Am. Mineral.*, **37**, 407-422.
- BUNN, C. W. (1946), *Chemical Crystallography*, Oxford, Clarendon Press, 422 p.
- EVANS, H. T., JR., AND BLOCK, S. (1953), The crystal structure of montroseite, a vanadium member of the diasporite group: *Am. Mineral.*, **38**, 1242-1250.
- FERSMAN, A. (1930), Geochemische migration der elemente, Teil II, I. Die Uran-Vanadinen Grube Tuja-Mujun in Turkestan: *Abh. prakt. geol. Bergwirtschaftslehre*, **19**, 1-52.
- HILLEBRAND, W. F., MERWIN, H. E., AND WRIGHT, F. E. (1941), Hewettite, metaheuwettite and pascoite, hydrous calcium vanadates: *Proc. Am. Phil. Soc.*, **53**, 31-54.
- NENADKOVICH, K. A. (1909), Turanite and alaite, two new vanadium minerals: *Acad. Sci. St. Petersburg Bull.*, **3**, ser. 6, 185-186.
- WEEKS, A. D., CISNEY, E. A., AND SHERWOOD, A. M. (1953), Montroseite, a new vanadium oxide from the Colorado Plateaus: *Am. Mineral.*, **38**, 1235-1241.
- WITKIND, I. J., JOHNSON, D. H., FINNELL, T. L., AND CLAUS, R. J. (1953), Geological investigations in the Monument Valley area, Arizona: *U. S. Geol. Survey Trace Elements Inv. Rept.* **204** (unpublished).

Manuscript received April 1, 1954.

REFINEMENT OF THE STRUCTURE OF CUBANITE, CuFe_2S_3

LEONID V. AZAROFF* AND M. J. BUEGER, *Crystallographic
Laboratory, Department of Geology and Geophysics,
Massachusetts Institute of Technology.*

ABSTRACT

The structure of cubanite, CuFe_2S_3 , was known from an earlier trial-and-error investigation. In this structure both iron and copper atoms are tetrahedrally coordinated to sulfur. The structure is peculiar in that the Fe tetrahedra share an edge giving rise to a short Fe-Fe distance which probably corresponds to a bond. Because of the ferromagnetism of cubanite it is important to know the details of the structure with accuracy. To this end the refining of the structure is herewith reported. The refining process was carried out in three stages: (1) by electron density projections, (2) by plane sections through the three-dimensional distribution of electron density, and (3) by difference line syntheses, $\rho_o - \rho_c$ through each atom. In the refined structure, the Fe atoms are found to be coordinated to four S atoms at distances of 2.29, 2.28, 2.27, 2.25 Å, and one Fe atom at 2.81 Å. The shared tetrahedral edge is somewhat shortened, having a length of 3.61 Å, as compared with the other edges of 3.71, 3.72, 3.73, 3.84, and 3.84 Å.

INTRODUCTION

The crystal structure of cubanite was determined by M. J. Buerger (1945, 1947). The metal atoms in this structure are tetrahedrally surrounded by sulfur atoms. The structure can be briefly described as slabs of the wurtzite arrangement parallel to (010) and averaging $b/2$ wide. These wurtzite-like slabs are joined to one another by inversion centers so that neighboring slabs have their tetrahedral apices reversed. The central portion of each slab is composed of copper tetrahedra and the sides of this slab are composed of iron tetrahedra. Since the inversion center occurs at a midpoint of an edge of an iron tetrahedron, it has the effect of joining all iron tetrahedra in pairs which share this edge. The sharing of tetrahedral edges is unusual, even in non-ionic crystals. It was only reasonable to suppose that the close approach of iron atoms across the shared tetrahedral edge corresponds to an Fe-Fe bond. This suggested that the iron atoms, in addition to being bonded to four sulfur atoms, are also bonded to one another in pairs.

Cubanite is one of the two ferromagnetic sulfide minerals. It has been suggested (Buerger, 1945) that the ferromagnetism may be related to the unusual coordination of iron. For this reason a detailed knowledge of the bond distances in cubanite is of more than routine interest. The original structure determination was carried out by trial-and-error methods, and, due to the limitations of the method, the accuracy of the

* Now with the solid-state section of the Armour Research Foundation, Chicago, Illinois.

published coordinates of the atoms is not known. Because of the bearing of the interatomic distances on the theory of ferromagnetism in cubanite, a refinement of the parameters of the structure was regarded as important. The details and results of the refinement investigation are reported here.

The space group of cubanite is $Pcmn$. The cell dimensions are as follows:

$$\begin{aligned}a &= 6.46 \text{ \AA} \\b &= 11.12 \\c &= 6.23\end{aligned}$$

This cell contains $4\text{CuFe}_2\text{S}_3$. The best coordinates found by the original trial-and-error search were as follows:

	x	y	z
Cu in $4c$:	$\sim \frac{7}{12}$	($\frac{1}{4}$)	.122
S _I in $4c$:	$\sim \frac{11}{12}$	($\frac{1}{4}$)	.270
Fe in $8d$:	$\sim \frac{1}{12}$.083	.135
S _{II} in $8d$:	$\sim \frac{5}{12}$.083	.265

EXPERIMENTAL PROCEDURE

Intensity determination. One of the crystals from the Frood Mine, Sudbury, Ontario, used for the original structure determination, was selected for intensity measurement. The crystal was mounted with its b axis parallel to the axis of the goniometer head and set on the precession (Buerger, 1944) camera. This mounting made it possible to take photographs of the $hk0$ and $0kl$ reflections with one mounting of the crystal. These reflections were recorded for $\text{MoK}\alpha$ radiation and the intensities were measured by using the M.I.T. modification of the Dawton (1938) method.

For crystals having orthorhombic symmetry, the entire three-dimensional reciprocal lattice can be recorded by the precession apparatus with a single mounting of the crystal. This is illustrated in Fig. 1. To accomplish this, one records zero and upper levels normal to the a and c axes as far as the range of the apparatus permits. The reflections missing due to the blind spot of the upper levels, and the reflections missing because they occur on the higher levels normal to each axis, are filled in by photographing the series of levels normal to $[\bar{1}01]$.

The symmetry of the reciprocal lattice combined with the repeated

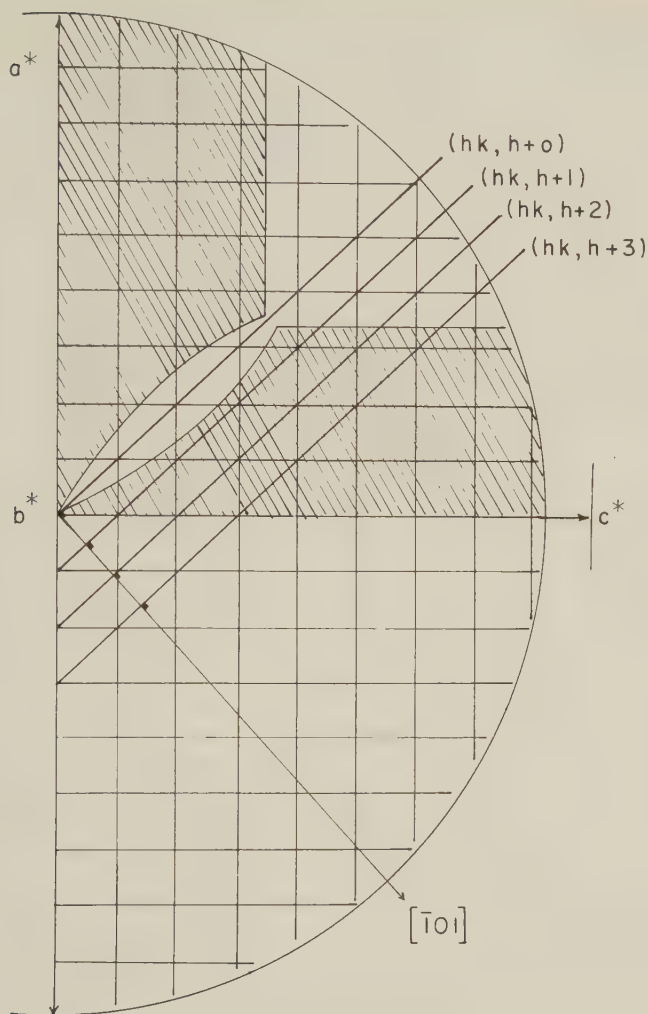


FIG. 1. Projection of reciprocal lattice of cubanite, showing regions explorable by precession photographs. Shaded areas are regions explorable by a axis and c axis precession photographs. Additional lines show how blind regions of a axis and c axis photographs can be filled in by $[101]$ axis precession photographs.

appearance of the same spots on more than one photograph provided the possibility of making four independent measurements of approximately 70% of the observable intensities. The remaining intensities were measured independently at least twice. The averages of these measurements were then used as the final observed intensities.

Correction of intensity. The intensities were corrected by applying the

Lorentz and polarization factors as determined for the zero-level precession photographs by Waser (1951) and upper levels by Burbank (1952) and Grenville-Wells and Abrahams (1952). The charts prepared by the above-mentioned authors were enlarged to a scale of 1 reciprocal lattice unit = 10 cm. and printed on transparent film. These films were then placed over a reciprocal-lattice net drawn to the same scale. The use of these enlarged charts and reciprocal-lattice nets rather than the original films allows a more accurate and rapid determination of the value of the correction.

The intensities were next corrected for absorption by the crystal. Since the crystal was an irregular, jagged fragment, an exact determination of the absorption correction was nearly impossible. An approximate

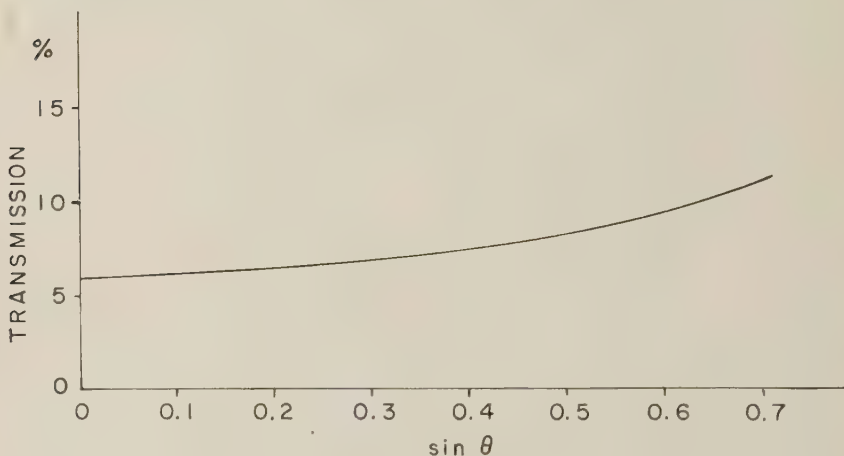


FIG. 2. Transmission of $\text{MoK}\alpha$ radiation by cubanite crystal used.

absorption correction based on the assumption that the crystal was spherical was therefore applied. Although this assumption is not strictly valid, it was felt that such an absorption correction would, nevertheless, appreciably decrease the errors in the observed intensities due to absorption effects.

The absorption corrections made were based on a method suggested by Ekstein and Evans (1951). The radius r of the sphere is first determined. In this case the average radius of the crystal ($r = 0.0175$ cm.) was used. The value of the radius is then multiplied by the linear absorption coefficient of the crystal, in this case $\mu = 127.5 \text{ cm}^{-1}$. The per cent transmission as a function of θ can then be determined by forming the product $\mu r = 2.23$, and referring to the above-cited tables. The tables list the per cent of x -radiation transmitted at the angles $\theta = 0^\circ$, $22\frac{1}{2}^\circ$, 45° , $67\frac{1}{2}^\circ$ and

90°. These values are then plotted and the best curve drawn through them. In this case the plot of transmissivity was made against $\sin \theta$ rather than θ as suggested by Evans (Ekstein and Evans, 1951), and is shown in Fig. 2. The absorption correction was then applied to the observed intensities by reading the per cent transmitted corresponding to the value of $\sin \theta$ for the reflection concerned and dividing the observed intensity by this value.

Finally, the square roots of the corrected intensities were taken and these values were used as the observed structure factors. The observed structure factors were placed on an absolute basis by plotting $|F_o|/|F_c|$ against $\sin^2 \theta$, Fig. 6. This plot not only determined the scale of the $|F_o|$'s but also the temperature factor ($B=1.63$) which was applied to the computed structure factors.

REFINEMENT OF COORDINATES

Outline of refinement procedure. The refinement was carried out in three stages. The first stage consisted of refinement by the electron-density

TABLE 1. COORDINATES OF ATOMS IN CUBANITE AT VARIOUS STAGES OF REFINEMENT

Atom	Coordinates Determined by									
	Original Trial- and- error Determi- nation	$\rho(yz)$		$\rho(x\frac{1}{4}z)$ and $\rho(x\frac{1}{2}z)$		First Difference Synthesis		Second Difference Synthesis		Param- eters Finally Accepted
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	
<i>x</i>	$\frac{1}{12}$.083 ₅	.085	.085	.087 ₅	.087 ₅	.087 ₅	.087 ₅
Fe <i>y</i>	.083	.083	.085			.085	.088	.088	.088	.088
<i>z</i>	.135	.135	.136	.136	.133	.133	.134	.134	.134	.134
<i>x</i>	$\frac{7}{12}$.583	.583	.583	.583	.583	.583	.583
Cu <i>y</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$			$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
<i>z</i>	.122	.122	.124	.124	.125	.125	.127	.127	.127	.127
<i>x</i>	$\frac{11}{12}$.916	.914	.914	.913	.913	.913	.913
Si <i>y</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$			$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
<i>z</i>	.270	.270	.264	.264	.263	.263	.262	.262	.262 ₅	.262 ₅
<i>x</i>	$\frac{5}{12}$.417	.415	.415	.413	.413	.413	.413
Si <i>y</i>	.083	.083	.084			.084	.083 ₅	.083 ₅	.083 ₅	.083 ₅
<i>z</i>	.265	.265	.274	.274	.274	.274	.274	.274	.274	.274
R:	22% 0kl	9.7% hkl 19 % 0kl		14% hkl		7.7% hkl 11 % 0kl		11.9% hkl		11.9% hkl

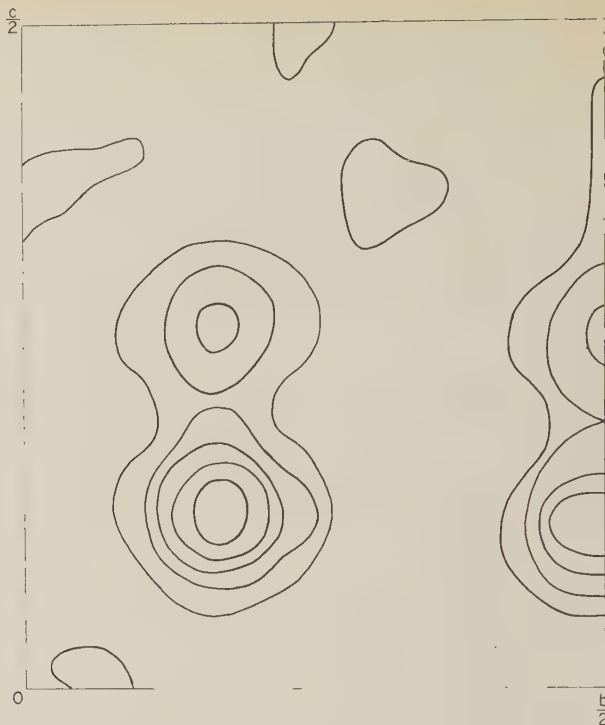


FIG. 3. Electron density projection, $\rho(yz)$, for cubanite.



FIG. 4. Electron density section, $\rho(x\frac{1}{2}z)$, for cubanite.



FIG. 5. Electron density section, $\rho(x\frac{1}{2}yz)$, for cubanite.

projection $\rho(yz)$. In the second stage the full set of hkl intensities was used to pass strategically located plane sections through the atoms. In the third stage the full set of three-dimensional intensities was used to pass 3 orthogonal lines through each atom. This last stage of the refinement was carried out by difference syntheses. The refinement procedure is outlined in Table 1. This table not only gives the change of coordinates produced by each stage of the refinement but also the final values of the residual factor, $R = (||F_o| - |F_c||) / |F_o|$, at each stage of the refinement.*

Refinement by projections. The coordinates of the atoms resulting from the trial-and-error structure determination, and listed in Table 1, were used as a starting point. The phases determined by these coordinates were applied to the observed amplitudes, F_{okl} , and the electron density $\rho(yz)$ was computed. This is shown in Fig. 3.

The atoms are quite well resolved in this projection. The coordinates of the peaks found in $\rho(yz)$ were used to compute a new set of structure

* In computing R , $F_o - F_o$ was omitted when $F_o = 0$.

factors. None of these new structure factors showed any change in phase, which indicated that no further refinement was possible by successive Fourier projections. At this point the residual factor for the $0kl$ reflections was 19%.

Of the three projections of the electron density on the pinacoids, only the projection on (100) can show all of the atoms resolved from one another for the cubanite structure. This means that the end point of refinement by projections had been reached by the preparation of the $\rho(yz)$ synthesis. However, the new coordinates determined by this projection were used to compute the structure factors of the hkl reflections. These proved to have the small residual factor of 9.7% which could hardly be improved.

Refinement by plane sections. The foregoing discussion makes it evident that any further refinement must come from employing all hkl reflections in some kind of three-dimensional Fourier synthesis. It will be observed from the tabulation of trial-and-error coordinates in Table 1 that the Cu and S_I atoms are confined to reflection planes with $y = \frac{1}{4}$, while the Fe and S_{II} atoms lie on planes having $y = .083 \approx 1/12$. This makes it possible to refine the x and z parameters by passing plane sections through the structure at $y = \frac{1}{4}$ and $y = 1/12$. Electron density syntheses corresponding to these sections were therefore prepared using

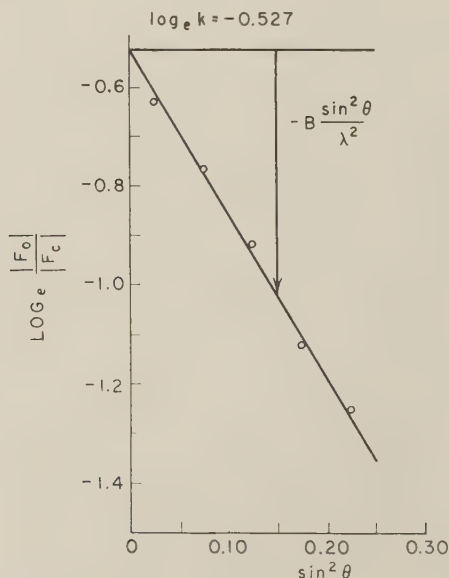


FIG. 6. Determination of absolute scale and temperature factor for cubanite.

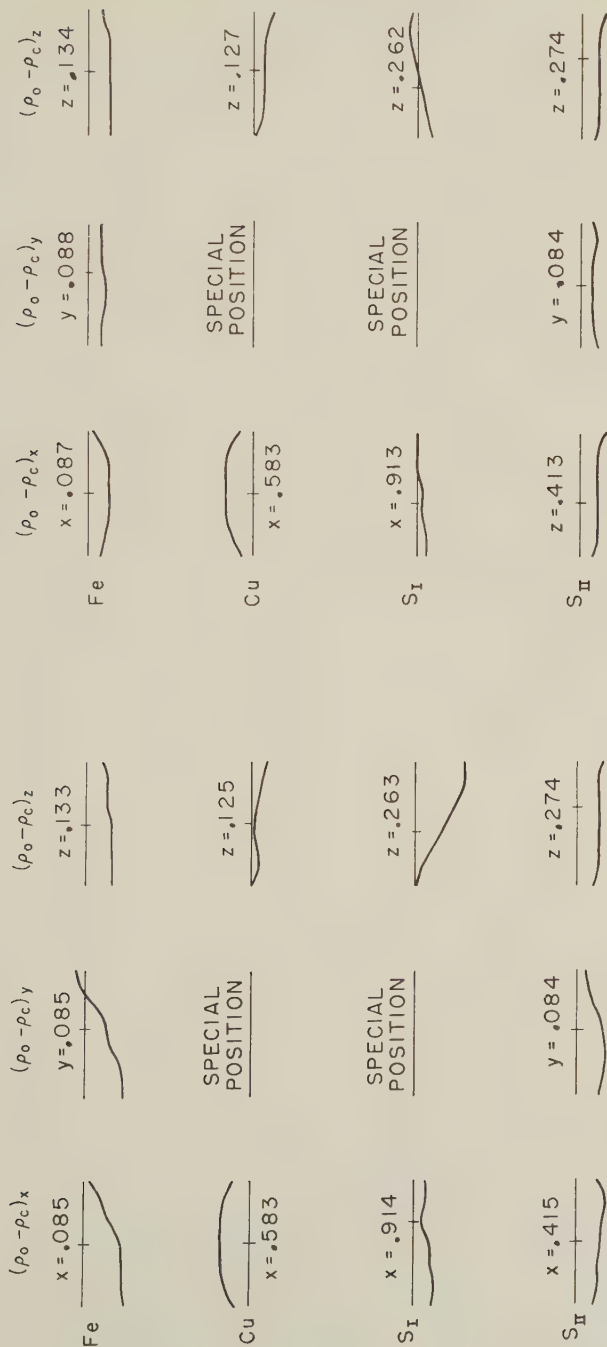


FIG. 7. First difference syntheses.

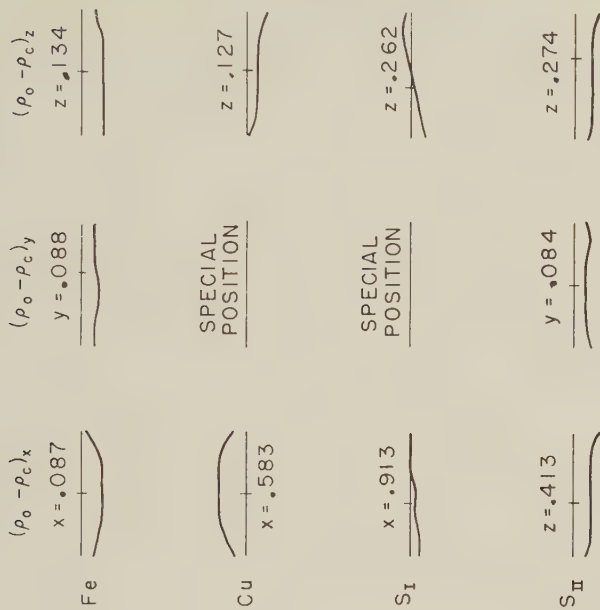


FIG. 8. Second difference syntheses.

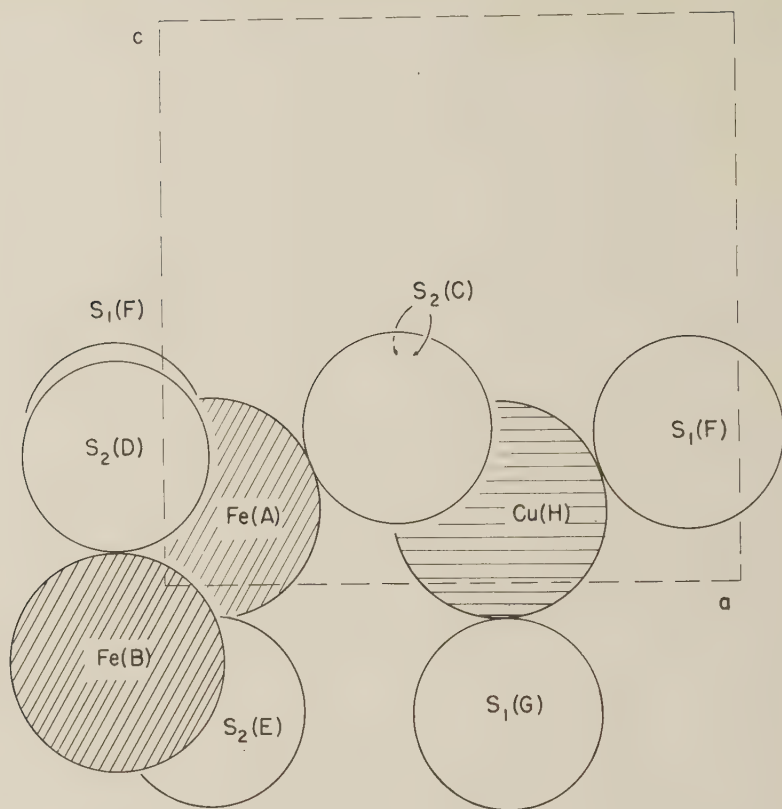


FIG. 9. Locations of atoms referred to in listing interatomic distances in cubanite.

the y and z parameters as refined by the projection $\rho(yz)$. These two syntheses are shown in Figs. 4 and 5. In these sections the atoms are clearly resolved. Their circular shapes suggest immediately that the phases are substantially correct. The coordinates obtained from these sections are tabulated in Table 1. The changes in coordinates over the last stage are very small indeed and correspond to no phase changes. The residual factor at this point for the entire three-dimensional set of intensities was 14%.

Refinement by difference syntheses. The shifts in atomic positions which had been encountered so far by the refinement procedure were so small that it could reasonably well be assumed that all atoms were near their final locations. The last stage in the refinement procedure was to study the atom locations as found in the foregoing stages by difference syntheses (Cochran, 1951). Since the atoms were substantially in their final positions, their centers could be readily located by passing three orthogonal lines (one parallel to each crystallographic axis) through each

TABLE 2. INTERATOMIC DISTANCES IN CUBANITE

Atom	Coordinates	Neighbor	Representative Coordinates	Bond Length
Fe(A)	x_1, y_1, z_1^*	Fe(B)	$\bar{x}_1, \bar{y}_1, \bar{z}_1^*$	2.80 ₈ Å
		S ₂ (C)	x_3, y_3, z_3	2.27 ₈ Å
		S ₂ (D)	$\frac{1}{2} + x_3, \bar{y}_3, \frac{1}{2} - z_3$	2.28 ₇ Å
		S ₂ (E)	$\frac{1}{2} - x_3, y_3, \frac{1}{2} + z_3$	2.24 ₅ Å
		S ₁ (F)	$x_4, \frac{1}{4}, z_4$	2.27 ₁ Å
Cu(H)	x_2, y_2, z_2	2S ₂ (C)	x_3, y_3, z_3	2.33 ₉ Å
		S ₁ (F)	$x_4, \frac{1}{4}, z_4$	2.29 ₂ Å
		S ₁ (G)	$\frac{1}{2} - x_4, \frac{1}{4}, \frac{1}{2} + z_4$	2.27 ₆ Å
S ₂ (C)	x_3, y_3, z_3	Fe(A)	x_1, y_1, z_1	2.27 ₈ Å
		Cu(H)	x_2, y_2, z_2	2.33 ₉ Å
		S ₂ (C)	$x_3, \frac{1}{2} - y_3, z_3$	3.70 ₂ Å
		S ₂ (E)	$\frac{1}{2} - x_3, y_3, \frac{1}{2} + z_3$	3.83 ₆ Å
		S ₁ (F)	$x_4, \frac{1}{4}, z_4$	3.72 ₄ Å
		S ₁ (G)	$\frac{1}{2} - x_4, \frac{1}{4}, \frac{1}{2} + z_4$	3.85 ₇ Å
S ₂ (D)	$\frac{1}{2} + x_3, \bar{y}_3, \frac{1}{2} - z_3$	Fe(A)	x_1, y_1, z_1	2.28 ₇ Å
		Fe(B)	$\bar{x}_1, \bar{y}_1, \bar{z}_1$	2.24 ₅ Å
		Fe	$\frac{1}{2} + x_1, \bar{y}_1, \frac{1}{2} - z_1$	2.27 ₈ Å
		S ₂ (C)	x_3, y_3, z_3	3.84 ₄ Å
		S ₂ (E)	$\frac{1}{2} - x_3, y_3, \frac{1}{2} + z_3$	3.61 Å
		S ₁ (F)	x_4, y_4, z_4	3.71 ₁ Å
S ₁ (F)	$x_4, \frac{1}{4}, z_4$	Cu(H)	$x_2, \frac{1}{4}, z_2$	2.29 ₂ Å
		Cu	$\frac{1}{2} - x_2, \frac{1}{4}, \frac{1}{2} + z_2$	2.27 ₅ Å
		2Fe(A)	x_1, y_1, z_1	2.27 ₁ Å
		S ₂ (E)	$\frac{1}{2} - x_3, y_3, \frac{1}{2} + z_3$	3.73 ₄ Å
		S ₁ (G)	$\frac{1}{2} - x_4, \frac{1}{4}, \frac{1}{2} + z_4$	3.76 ₂ Å

* The subscripts 1, 2, 3, 4 refer to the coordinates of Fe, Cu, S_{II}, S_I respectively, as tabulated in Table 1.

atom. Difference electron densities, $D = \rho_o - \rho_c$, were computed along each of these lines. The x and z coordinates used for ρ_c were thus given by $\rho(x\frac{1}{4}z)$ and $\rho(x\frac{1}{2}z)$ while the y coordinates were thus given by $\rho(yz)$. These coordinates were used to prepare computed values of the complete set of F_{hkl} 's. The ρ_o component of the synthesis was prepared by using observed F_{hkl} 's and the signs given by the computed F_{hkl} 's. The actual Fourier series were computed with the help of *ODFAC* (Azaroff, 1954), a one-dimensional computer built in this laboratory.

The criterion for the correctness of an atom location is that it should lie on the zero gradient of the difference synthesis. The first set of difference syntheses is shown in Fig. 7. Atoms lying on gradients were moved

TABLE 3. INTERATOMIC BOND ANGLES IN CUBANITE

Bonded Atoms	Angle
$S_2(D)-Fe-S_2(E)$	$105^\circ 36'$
$S_2(C)-Fe-S_1(F)$	$109^\circ 57'$
$S_2(C)-Fe-S_2(D)$	$114^\circ 44'$
$S_1(F)-Fe-S_2(E)$	$111^\circ 35'$
$S_2(C)-Cu-S_2(C)$	$104^\circ 38'$
$S_2(C)-Cu-S_1(F)$	$107^\circ 03'$
$S_1(F)-Cu-S_1(G)$	$110^\circ 54'$
$S_2(C)-Cu-S_1(G)$	$113^\circ 12'$

up the gradient and the second difference syntheses were prepared using these new coordinates. This second set is shown in Fig. 8. In this new difference synthesis all atoms appear to be on substantially zero gradient except for the z coordinate of S_1 . In view of the fact that the gradient of the z difference synthesis for this atom changed direction it could be safely assumed that the atom lies between the parameter values assumed in computing these two sets of syntheses. The final set of parameters accepted for the structure is listed in the last column of Table 1. The R value had now been reduced to less than 12% for all hkl reflections. A comparison of observed and computed F values is now on file with the American Documentary Institute.*

INTERATOMIC DISTANCES IN THE STRUCTURE

The distances between atoms for the parameters found for the refined structure are listed in Table 2. In this table the designations (A), (B), etc., refer to the particular atoms so labelled in Fig. 9. The angles between the bonds are listed in Table 3.

It is interesting to examine the environment of the Fe atom (A). This atom is surrounded by four sulfur atoms, namely (C), (D), (E), and (F), at distances of 2.28, 2.29, 2.25 and 2.27 Å. The Fe atom (B), across the shared edge, is at a distance of 2.81 Å. This distance is longer than any of the customary Fe-Fe bond distances and yet much shorter than what would be expected if the Fe's were unbonded. The shared edge between these atoms has a length of 3.61 Å which is shorter than the other S-S distances (3.71, 3.72, 3.73, 3.84, and 3.84 Å) in the Fe tetrahedra. Ordinarily such a shortening of a shared edge would be attributed to an ionic component of the Fe atoms, but in this case it would appear

* A copy may be secured by writing to the *ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C.*, and requesting Document number **4190**. Advance payment of \$1.25 is required for photoprints, or \$1.25 for 35 mm. microfilm. Make checks payable to: Chief, Photoduplication service, Library of Congress.

TABLE 4. CHARACTERISTICS OF COORDINATION TETRAHEDRA IN CUBANITE

Environment of Fe(A)	Environment of Cu(H)
S ₂ (E) 2.25 Å	S ₁ (G) 2.28 Å
S ₁ (F) 2.27	S ₁ (F) 2.29
S ₂ (C) 2.28	S ₂ (C) $\left\{ \begin{array}{l} 2.34 \\ 2.34 \end{array} \right.$
S ₂ (D) 2.29	
Fe(B) 2.81	
Tetrahedral Edges	Tetrahedral Edges
shared edge: 3.61 DE	3.70 CC
3.71 DF	3.72 $\left. \begin{array}{l} \text{CF} \\ \text{CF} \end{array} \right\}$
3.72 CF	3.72 $\left. \begin{array}{l} \text{FG} \\ \text{CG} \end{array} \right\}$
3.73 EF	3.76 FG
3.84 CD	3.86 $\left. \begin{array}{l} \text{CG} \\ \text{CG} \end{array} \right\}$
3.84 CE	3.86 $\left. \begin{array}{l} \text{CG} \\ \text{CG} \end{array} \right\}$

that a more reasonable interpretation is merely that it is due to the repulsion of those parts of the electronic clouds of the two atoms which are not involved in the Fe-Fe bond formation.

ACKNOWLEDGMENT

This research was supported by the Office of Naval Research under Contract No. *N5ori-07860* with the Massachusetts Institute of Technology.

REFERENCES

- AZAROFF, LEONID V. (1954), A one-dimensional Fourier analogue computer: *Rev. Sci. Inst.*, **25**, 471-477.
- BUERGER, M. J. (1944), The Photography of the Reciprocal Lattice. *ASXRED Monograph No. 1*.
- BUERGER, M. J. (1945), The structure of cubanite, CuFe_3S_3 , and the coordination of ferromagnetic iron: *J. Am. Chem. Soc.*, **67**, 2056.
- BUERGER, M. J. (1947), The crystal structure of cubanite: *Am. Mineral.*, **32**, 415-425.
- BURBANK, R. D. (1952), Upper level precession photography and the Lorentz-polarization correction, Part I: *Rev. Sci. Inst.*, **23**, 321-327.
- COCHRAN, W. (1951), The structures of pyrimidines and purines. V. The electron distribution in adenine hydrochloride: *Acta Cryst.*, **4**, 81-92.
- DAWTON, R. H. V. M. (1938), The integration of large numbers of x-ray reflections: *Proc. Phys. Soc.*, **50**, 919-925.
- EVANS, H. T., JR., and EKSTEIN, MIRIAM (1952), Tables of absorption factors for spherical crystals: *Acta Cryst.*, **5**, 540-542.
- GRENVILLE-WELLS, H. J., and ABRAHAMS, S. C. (1952), Upper level precession photography and the Lorentz-polarization correction, Part II: *Rev. Sci. Inst.*, **23**, 328-331.
- WASER, J. (1951), The Lorentz factor for the Buerger precession method: *Rev. Sci. Inst.*, **22**, 567-568.

THE CRYSTAL STRUCTURE OF BERTHIERITE, FeSb_2S_4

M. J. BUEGER AND THEODOR HAHN, *Crystallographic Laboratory,
Department of Geology and Geophysics, Massachusetts Institute
of Technology, Cambridge, Massachusetts.*

ABSTRACT

The general arrangement of atoms in berthierite had been suggested in an earlier publication by solving the Patterson function $P(xy)$, with the aid of the minimum function $M_s(xy)$. In this paper a report is given of the refinement of the structure. The intensities were measured by the M.I.T. modification of the Dawton method, and the resulting F^{2s} were placed on an absolute basis by Wilson's method. The structure was refined by the use of successive difference Fourier syntheses. The final structure has a small residual factor and neatly reproduces the Patterson projection.

In the structure of berthierite each Sb atom is evidently bonded to 3 S atoms at distances of about 2.5 Å. These SbS_3 groups share S atoms to form two non-equivalent SbS_2 chains parallel to the c axis. The Fe atoms are surrounded by 6 S atoms in approximately octahedral arrangement at distances of about 2.5 Å. This is about the expected distance for ionic Fe-S bonds. The structure can therefore probably be regarded as $\text{Fe}^{++}(\text{SbS}_2)_2^-$.

INTRODUCTION

Material. The berthierite from Kisbánya, Carpathians, has been described in detail by Zsivny and Zombory (1934). These investigators were kind enough to make a generous sample of this material available for this crystal-structure investigation. The analysis of the Kisbánya berthierite indicates that it has almost exactly the ideal composition FeSb_2S_4 .

Unit cell and space group. The unit cell and space group of berthierite have been reported in an earlier communication (Buerger, 1936). The cell has the following dimensions:

$$a = 11.44 \text{ Å}$$

$$b = 14.12$$

$$c = 3.76$$

This cell contains $4\text{FeSb}_2\text{S}_4$. The space group is $Pnam$.

Intensity determination. The structure determination reported here was based upon $hk0$ and $h0l$ reflections as recorded on precession photographs. The intensities were determined by using the M.I.T. modification of the Dawton (1938) method. The intensities were corrected for Lorentz and polarization factors, but no allowance was made for absorption.

In the course of the structure determination it became evident that the F values determined in this manner were accurate and quite satisfactory except that there is a critical lower intensity below which one cannot distinguish a non-zero intensity from zero intensity. The lack of knowledge of the F 's having amplitudes between zero and the lowest observable amplitude was keenly felt as the refinement progressed.

TABLE 1. COORDINATES OF ATOMS FOR DIFFERENT TRIALS

		Trial										
		1	2	3	4	5	6	7	8	9	10	11
Sb _I	<i>x</i>	.147	.148	.149	.149	.149	.148	.145	.140	.143	.145	.145
	<i>y</i>	.060	.059	.059	.063	.063	.063	.064	.063	.063	.062	.062
Sb _{II}	<i>x</i>	.040	.044	.041	.037	.037	.038	.036	.041	.039	.037	.037
	<i>y</i>	.384	.382	.381	.387	.387	.386	.385	.386	.386	.386	.386
Fe	<i>x</i>	.321	.318	.318	.323	.323	.321	.314	.320	.316	.316	.317
	<i>y</i>	.340	.336	.337	.339	.339	.337	.335	.335	.334	.334	.335
S _I	<i>x</i>	.190	.204	.200	.230	.200	.200	.197	.197	.196	.195	.194
	<i>y</i>	.270	.273	.273	.290	.273	.270	.272	.272	.272	.272	.272
S _{II}	<i>x</i>	.414	.419	.421	.417	.421	.424	.428	.428	.426	.424	.423
	<i>y</i>	.200	.186	.187	.198	.187	.185	.186	.186	.185	.184	.185
S _{III}	<i>x</i>	.240	.229	.230	.237	.230	.227	.229	.229	.227	.226	.226
	<i>y</i>	.485	.495	.494	.484	.494	.493	.494	.494	.492	.492	.492
S _{IV}	<i>x</i>	.452	.452	.450	.418	.450	.451	.452	.452	.450	.451	.451
	<i>y</i>	.408	.407	.407	.388	.407	.404	.405	.405	.406	.405	.405

TABLE 2. *R* FACTORS FOR F_{hko} FOR DIFFERENT TRIALS

		3	4	5	6	7	8	9	10	11
R, %	(a)	19.0	27.3	17.1	14.7	15.8 14.2*	14.3*	12.4*	12.8*	13.2*
	(b)	17.8	26.4	16.0	12.6	13.2 12.3*	12.2*	10.2*	10.8*	11.1*
	(c)	24.5	38.5	22.5	19.1	19.8 18.6*	19.3*	16.8*	17.1*	17.3*
	(d)	23.3	37.4	19.8	17.2	17.6 16.8*	17.2*	14.7*	15.1*	15.3*

(a) $\Delta F = F_o - F_c$ omitted if $F_o = 0$.(b) $\Delta F = F_o - F_c$ omitted if $\Delta \leq$ least significant difference.(c) When $F_o = 0$, it is assigned a mean value between true zero and least observable F_o .(d) Condition *b* and *c* together.

* New scale.

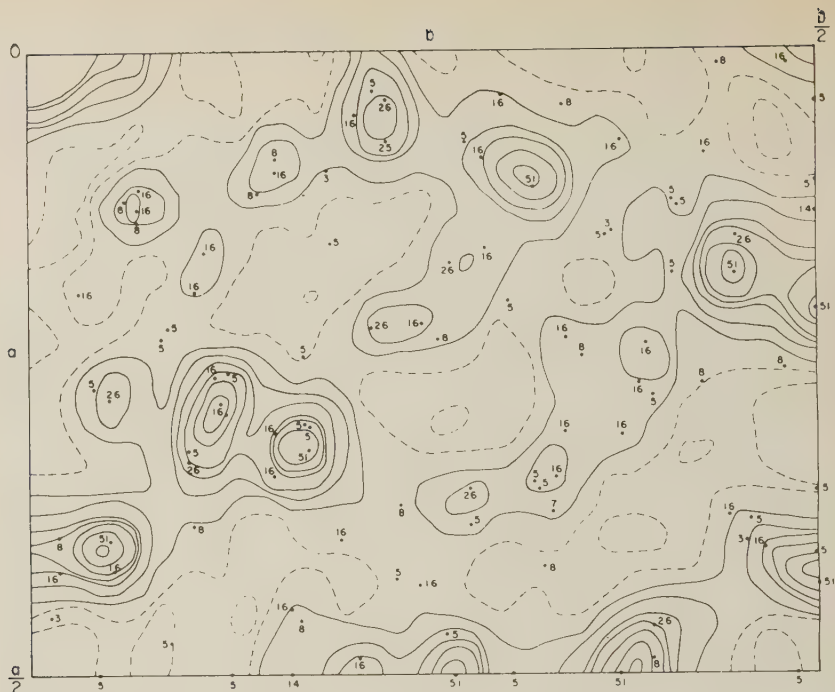


FIG. 1. Patterson projection of berthierite, $P(xy)$. Dots and accompanying numbers show weighted vector set for the final structure.

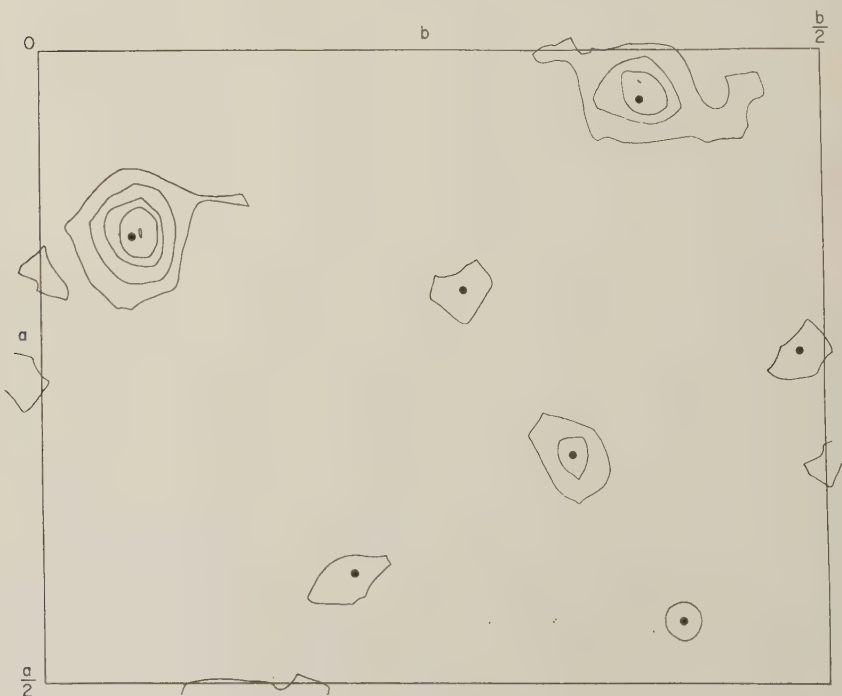


FIG. 2. The minimum function, M_s . Dots show the positions of the atoms as derived from the minimum function.



FIG. 3. The electron density map, $\rho(xy)$ of berthierite.

APPROXIMATE LOCATIONS OF ATOMS

Rough intensity considerations had already shown that all atoms of berthierite were confined to the (001) reflection planes, that is, to equi-point $4c$, for which $z = \pm \frac{1}{4}$. With the aid of the F^2_{hko} 's, a Patterson projection $P(xy)$ was prepared, Fig. 1. In another place (Buerger, 1951) it was shown that this projection could be solved for the xy coordinates of the atoms by applying the minimum function (Buerger, 1950). The approximate electron density found by this method is shown in Fig. 2. The several dense areas, in order of decreasing density, are evidently the two antimony atoms, the one iron atom, and the four sulfur atoms. The close relation of this minimum function map to the true structure can be appreciated by comparing it with Fig. 3, the electron density projection $\rho(xy)$, as determined after refinement.

There is an interesting peculiarity about an approximate structure determined by image-seeking methods: one must make a decision regarding the location of at least the first image point. The location of the one atom corresponding to this image point is fixed by this choice and

does not change in the course of applying the image-seeking function to find the other atoms of the structure. There is usually a small error involved in selecting an image point. For example, an error arises when the Patterson peak chosen for the image point is not a single peak, but rather the coalescence of several peaks not in exactly the same location. At this stage of the analysis one cannot usually determine to what extent the peak is composite. This image-point error remains as a slight error in the location of the corresponding atom. The error can only be removed by a subsequent refinement process.

PRELIMINARY REFINEMENT

The structure of berthierite as found by image-seeking methods was believed to be essentially correct with regard to the general location of the atoms, since there was a rough agreement between computed and observed intensities. Nevertheless this agreement was not good. Refinement of this structure was evidently necessary. It was carried out in

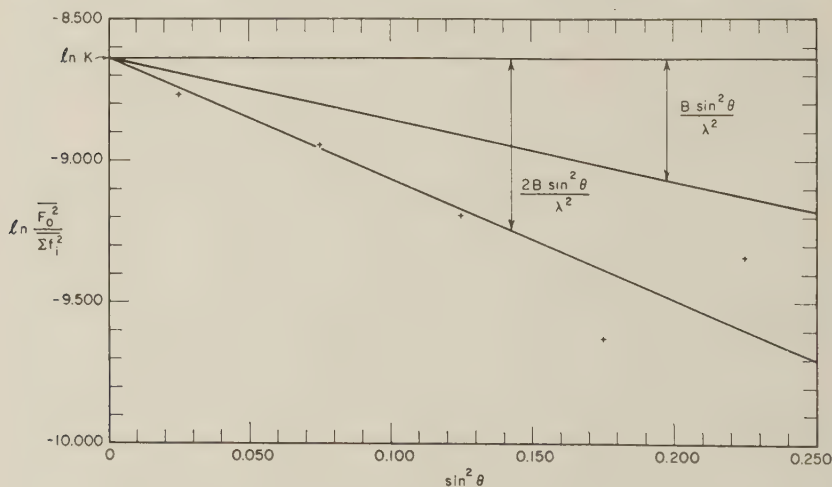


FIG. 4. Determination of absolute scale and temperature factor for F_{hk0} by Wilson's method.

eleven stages. The migration of coordinates during the refinement is outlined in Table 1.

For the purpose of refining the structure, the observed $hk0$ intensities were placed on an absolute basis using Wilson's (1942) method, Fig. 4. This analysis not only places the intensities on an absolute basis but also yields the temperature coefficient B . The value of this turned out to be 1.07 \AA^2 for berthierite. The value of B and the absolute scale of intensi-

ties were slightly improved when the structure was considerably refined.

The original structure as determined with the aid of the minimum function was termed *trial 1*. This was examined to ascertain what obvious shifts in atom locations would improve agreement between calculated and observed intensities. This predicted an improved set of atom locations which was called *trial 2*. This procedure was repeated, resulting in an improved set of atom locations called *trial 3*.

FURTHER REFINEMENT

Residual factor. This marked the end of elementary methods of refining the structure. From this stage onward, the status of the refinement was followed by computing the observed and computed amplitude residual factor (Robertson and Woodward, 1936)

$$R = \frac{\sum ||F_{\text{observed}}| - |F_{\text{calculated}}||}{\sum |F_{\text{observed}}|} \quad (1)$$

The magnitude of this factor varies somewhat depending upon how one treats the smallest F_o and the smallest differences, $\Delta = F_o - F_c$. In Table 2 we have computed four types of R , labelled (a), (b), (c), and (d). These are defined in Table 2.

Refinement by Patterson maps. The first non-elementary refinement procedure made use of comparing the weighted vector set of trial 3 with the observed Patterson map. These showed reasonably good agreement, but

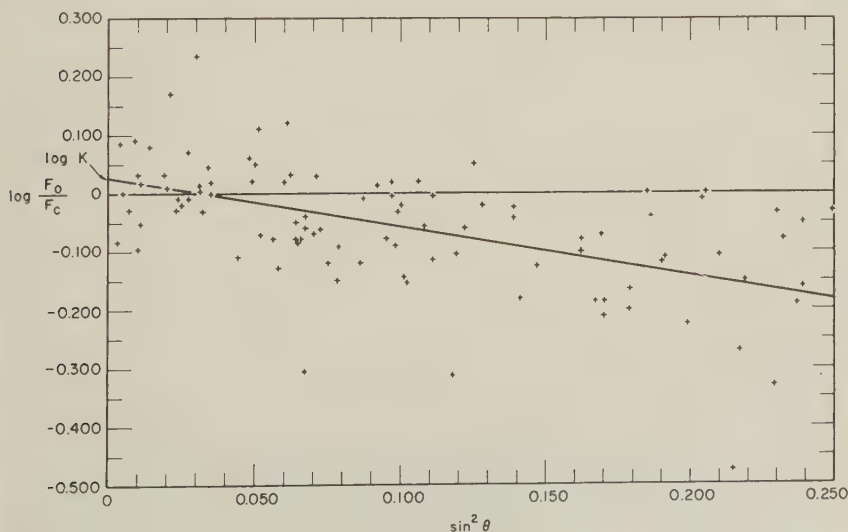


FIG. 5. Final refinement of absolute scale of F_{hk0} of berthierite.

detailed comparison indicated that the agreement could be improved by some small shifts in the locations of some atoms. This improved structure was termed *trial 5*. Another set of atom locations, called *trial 4*, differs from trial 5 only in that the sulfur atoms had been moved to idealized covalent octahedral locations about iron. Table 1 shows that the residual factor for the ideal sulfur arrangement was so much worse that the possibility of an idealized FeS_6 group was evidently excluded.

From this point on the structure was refined chiefly by difference syntheses (Cochran, 1951), using as Fourier coefficients $(F_{\text{observed}} - F_{\text{computed}})_{hkl}$. This synthesis is known to minimize R .

First difference synthesis. The set of amplitudes F_c , computed from trial 5 (resulting from the refinement-by-Patterson procedure) was used to compute a difference synthesis, Fig. 6. The atom locations proved to be on gradients on this map, so the locations were shifted up-gradient to produce a new set of locations, namely *trial 6*. The change from trial 5 to trial 6 reduced the residual factor from 17.1% to 14.7%.

Electron density projection, $\rho(xy)$. At this point it was believed that the structure was in a sufficient state of refinement to warrant preparing an electron density projection, $\rho(xy)$. This shown in Fig. 3. The peak locations of $\rho(xy)$ are taken as *trial 7*. Although the coordinates of trial 6 and trial 7 are different, they do not correspond to any changes in phase of F_{hkl} . Thus Fig. 3 may be taken as the final electron density map. The weighted vector set of trial 7 is shown superposed on the corresponding Patterson map in Fig. 1. The agreement between them is quite good, so that the structure may be said to neatly explain the Patterson synthesis.

In spite of the fact that Fig. 3 is the final $\rho(xy)$, the locations of its peaks do not provide the best values of the coordinates. This is obvious on studying Table 1. Trial 7 has a larger R value than trial 6. Furthermore, starting with trial 7, whose coordinates are derived from $\rho(xy)$, it is possible to obtain other sets of coordinates by refinement which have smaller R values, and without changing the phases of any F_{hkl} 's. That a set of F_{hkl} 's produces a map, $\rho(xy)$, whose peaks deviate slightly from the exact atom locations is due to using a finite set of F_{hkl} 's in the synthesis. This is the series-termination effect. This effect is substantially absent in differential syntheses. The residual termination effect does not change the general course of the lines of the difference map, and consequently the gradient is insensitive to slight errors in the F 's. On the other hand a peak maximum in $\rho(xz)$ is, in general, shifted by the termination effect. The study given here presents detailed evidence that difference syntheses are superior to electron-density syntheses for refinement.

New scale factor. Up to this point the scale factor derived by Wilson's method had been used. Since no further sign changes were in prospect,

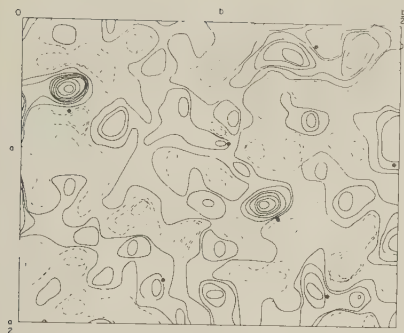


FIG. 6

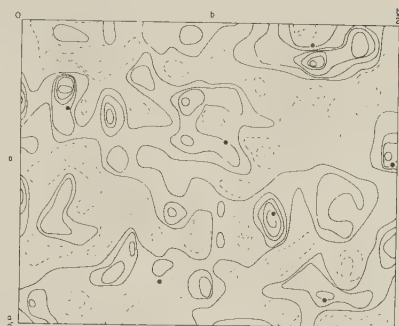


FIG. 7

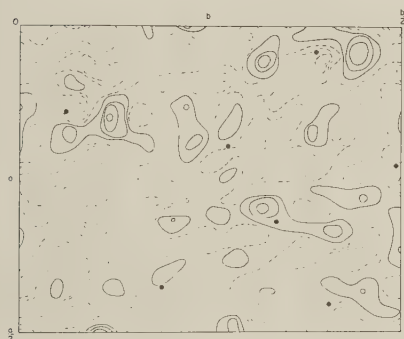


FIG. 8

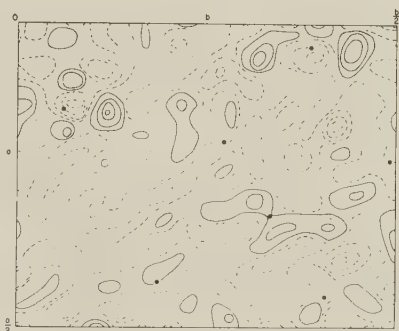


FIG. 9

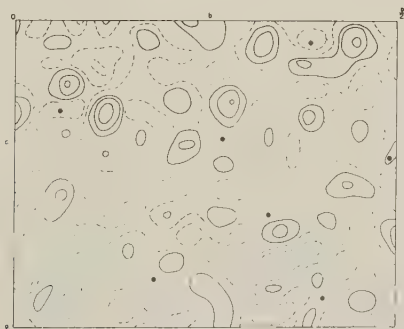


FIG. 10

FIGS. 6, 7, 8, 9, 10. Difference maps, $\rho_o - \rho_c$, for successive trial structures. The positions of atoms used for the ρ_c part of the particular difference map are shown by dots.

the structure was regarded as sufficiently well-settled to permit computing a new refined scale factor, by plotting $\log |F_o| / |F_c|$ against $\sin^2 \theta$. This is shown in Fig. 5. The change in the scale factor in going from

Wilson's method to this method proved to be from 75.5 to 71.0, while B changed from 1.07 \AA^2 to 0.98 \AA^2 . The use of the new scale factor reduced the R factor from 15.8% to 14.2%.

Further refinement by difference synthesis. Trial 7 was further refined by a series of difference syntheses shown in Figs. 7, 8, 9, and 10. In these figures the atom locations used for the difference syntheses are shown as black dots. The criterion for correct atom position is that the original atom locations are found to lie on positions of zero gradient on the difference map. In each trial, therefore, the dots were moved up-gradient in the hope that the subsequent synthesis would show them to lie on zero gradient.

In order to find the parameter range within which the Sb's must lie, these were moved by .005 from trial 7 to trial 8. This move proved to be too much, as indicated by the sharp reversal of gradient which accompanied the shift. Subsequent trials have Sb parameters between the values used for trial 7 and trial 8.

The Fe and three of the S atoms assumed positions of substantially zero gradient by trial 9. In trial 10 the other atoms are also in zero-gradient position but the Fe atom again appears to lie on a slight gradient. This is probably due to contributions from other atoms and therefore signifies that refinement of the Fe position has been achieved within the accuracy of our data. Trial 11 was devised to give the Fe and 2 S's a slight shift to improve their positions on gradients. This last set of shifts produced a set of parameters having higher R values. Trial 10 was accordingly accepted as the final set of parameters since the atoms are all on substantially zero gradient even though its R value is slightly greater than that of trial 9.

After computing this set of difference syntheses, it became evident that a shift of parameters of .001 or .002 changes the configuration of the map strongly and in such a way as to reverse the gradient, at least for the heavier atoms when they are in the neighborhood of the correct locations. From this it is deduced that the accuracy of the final atomic coordinates given for berthierite is about .002, which is equivalent to about .02 Å. It is of interest to note that when the atoms are in the neighborhood of their final correct positions the major features of the difference map coincide with the background of the electron density map. The features of the difference map must, therefore, be regarded as due chiefly to errors in the determination of the F_o 's.

SELECTION OF z PARAMETERS

The xy coordinates of all atoms in the structure are now known with accuracy. Since the atoms are confined to the reflection planes, their co-

TABLE 3. *R* FACTORS FOR F_{h0l}

(a)	8.8%
(b)	5.9%
(c)	8.8%
(d)	5.9%

(See Table 2 for explanation of conditions *a*, *b*, *c*, and *d*.)

ordinates can be either $\frac{1}{4}$ or $-\frac{1}{4}$. The only combination which was acceptable was found by making a limited number of intensity computations for F_{h0l} . A complete set of F_{h0l} 's was computed based upon this combination. These were independently placed on an absolute basis by comparing observed and computed intensities. The resulting temperature factor, *B*, for the $h0l$ reflections proved to be 0.99, compared with 0.98 found previously for the $hk0$ reflections. The resulting *R* values are shown in Table 3. The electron-density projection $\rho(xz)$ is shown in Fig. 11. In this projection some of the atoms are unresolved due to overlapping.

THE FINAL STRUCTURE

The electron density projections for the entire cell are shown in proper relation in Fig. 12. The final parameters are given in Table 4. A comparison of observed and computed *F* values is filed with the American Documentary Institute.*

DISCUSSION OF THE STRUCTURE

The distances between neighboring atoms in berthierite are listed in Table 5. These distances are shown in a diagrammatic representation of the structure in Fig. 13.

It is convenient to discuss the structure of berthierite in two stages. In the first stage account is taken only of the nearest neighbors. Table 5 and Fig. 13 show that each of the two kinds of Sb atoms has three

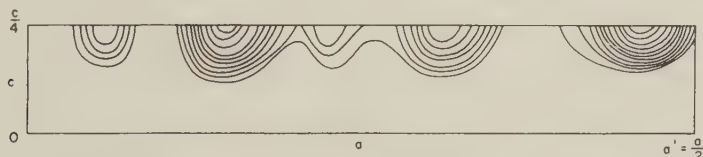


FIG. 11. The electron density map $\rho(xz)$ of berthierite.

* A copy may be secured by writing to the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., and requesting Document number 4189. Advance payment of \$1.25 is required for photoprints, or \$1.25 for 35 mm. microfilm. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

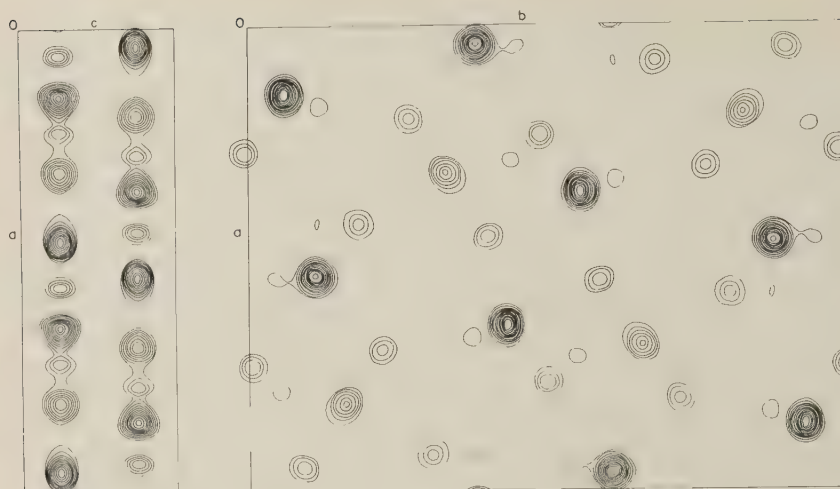


FIG. 12. Relation between the electron density projections $\rho(xy)$ (right), and $\rho(xz)$ (left), for the full cell of berthierite.

nearest S neighbors at distances of about 2.5 Å, as well as other S atoms at larger distances. The Sb and S atoms thus form SbS_3 groups. Each group shares two of its three S atoms with translation-equivalent groups to form SbS_2 chains parallel to the c axis.

The Fe atoms are surrounded by six S atoms in approximately octahedral arrangement. These octahedra share edges to form chains parallel to the c axis. The Fe-S distance is about 2.5 Å. This is considerably in excess of that found in structures where the bonds are recognized as covalent (pyrite, 2.26 Å, marcasite, 2.24 Å). The distance is about what would be expected for ionic Fe-S bonds. Thus, the structure of berthierite suggests that its chemical nature is $\text{Fe}^{++}(\text{SbS}_2)_2^-$. Curiously enough, the Sb_I triangles share an edge with each of two neighboring Fe octahedra, whereas the Sb_II triangles only share corners with these octahedra.

TABLE 4. FINAL COORDINATES OF ATOMS IN BERTHIERITE

	x	y	z
Sb_I	0.145	0.062	$+\frac{1}{4}$
Sb_II	0.037	0.386	$-\frac{1}{4}$
Fe	0.316	0.334	$+\frac{1}{4}$
S_I	0.195	0.272	$-\frac{1}{4}$
S_II	0.424	0.184	$+\frac{1}{4}$
S_III	0.226	0.492	$+\frac{1}{4}$
S_IV	0.451	0.405	$-\frac{1}{4}$

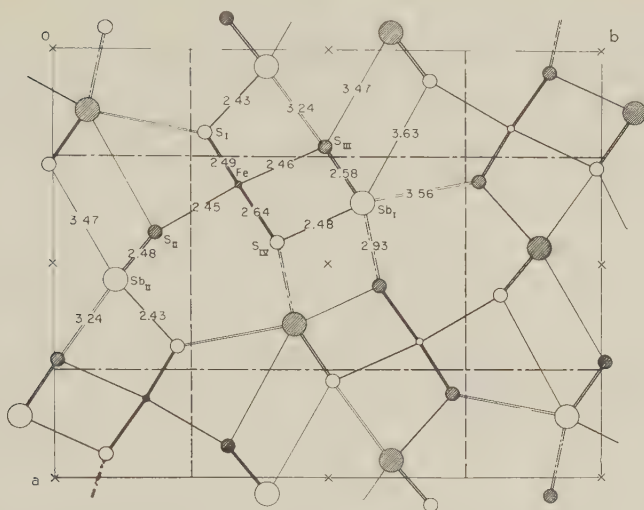


FIG. 13. Interatomic distances in berthierite. Shaded circles represent atoms on level $+\frac{1}{4}$, while open circles represent atoms on level $-\frac{1}{4}$.

Each of the four kinds of sulfur atoms in berthierite is coordinated to three metal atoms and each such set of metals contains both Fe and Sb atoms.

If one takes account of second small inter-atomic distances then it becomes evident that the two kinds of Sb atoms are quite different. The Sb_{II} has no further neighbors nearer than 3.2 Å while Sb_I has two additional neighbors at about 2.9 Å. This rather small distance doubtless represents a bond, so that one can also describe the Sb_I atoms as forming irregular SbS₅ groups. Two such SbS₅ groups, related by the inversion center in the middle of Fig. 13, share the two second-nearest S's with

TABLE 5. INTERATOMIC DISTANCES IN BERTHIERITE

	S _I	S _{II}	S _{III}	S _{IV}
Sb _I	3.56 (2)	3.63 (1)	2.58 (2)	$\begin{cases} 2.48 (1) \\ 2.93 (2) \end{cases}$
Sb _{II}	2.43 (1)	2.48 (2)	$\begin{cases} 3.24 (2) \\ 3.47 (1) \end{cases}$	
Fe	2.49 (2)	2.45 (1)	2.46 (1)	2.64 (2)
S _I	3.76 (2)	3.45 (2)	3.64 (2)	
S _{II}		3.76 (2)		3.66 (2)
S _{III}			3.76 (2)	3.43 (2)
S _{IV}				3.76 (2)

Note: Numbers in parentheses indicate the number of distinct vectors of this length.

each other so that a complex chain of composition Sb_2S_4 can be discerned parallel to the c axis. An alternative description is that the two SbS_2 chains, related by the inversion center in the middle of Fig. 13, can be regarded as joined so as to form more complex chains of composition Sb_2S_4 . This kind of double chain has also been discovered in livingstonite (Buerger and Niizeki, 1954). The two kinds of sulfur coordination displayed by Sb_{II} and Sb_{I} atoms are also found in the two types of Sb atoms of stibnite.

The Fe atom appears to have the function of cementing together the two kinds of SbS_2 chains. It should be noted that the coordination of Fe is irregular octahedral. Four of the S atoms are at distances of about 2.46 Å but two more are at distances of 2.64 Å. This condition is quite real since an attempt to regularize the distances resulted in a much higher R value.

The cleavage of berthierite is reported in one reference as more or less distinct parallel to one pinacoid, and in another reference as rather distinct prismatic. Fig. 13 shows that a cleavage could occur parallel to (010) without the breaking of any bonds except the 2.93 Å bond from Sb_{I} to S_{IV} .

ACKNOWLEDGMENT

This research was supported by the Office of Naval Research under Contract No. *N5ori-07860* with the Massachusetts Institute of Technology.

REFERENCES

- BUERGER, M. J. (1936), Crystallographic data, unit cell and space group for berthierite (FeSb_2S_4): *Am. Mineral.*, **21**, 442–448.
- BUERGER, M. J. (1950), Limitation of electron density by the Patterson function: *Proc. Nat. Acad. Sci.*, **36**, 738–742.
- BUERGER, M. J. (1951), A new approach to crystal-structure analysis: *Acta Cryst.*, **4**, 531–544.
- BUERGER, M. J., AND NIIZEKI, NOBUKAZU (1954), The crystal structure of livingstonite, HgSb_4S_7 : *Am. Mineral.*, **39**, 319–320.
- COCHRAN, W. (1951), The structures of pyrimidines and purines. V. The electron distribution in adenine hydrochloride: *Acta Cryst.*, **4**, 81–92.
- DAWTON, RALPH H. V. M. (1938), The integration of large numbers of x -ray reflections: *Proc. Phys. Soc.*, **50**, 919–925.
- ROBERTSON, J. MONTEATH, AND WOODWARD, IDA (1936), The structure of the carboxyl group. A quantitative investigation of oxalic acid dihydrate by Fourier synthesis from the x -ray crystal data: *J. Chem. Soc. Lond.*, 1817–1824, esp. p. 1822.
- WILSON, A. J. C. (1942), Determination of absolute from relative x -ray intensity data: *Nature*, **150**, 151–152.
- ZSIVNY, VICTOR, AND ZOMBORY, LÁSZLÓ (1934), Berthierite from Kisbánya, Carpathians: *Mineral. Mag.*, **23**, 566–568.

Manuscript received Jan. 20, 1954.

STEVENSITE, A MONTMORILLONITE-TYPE MINERAL SHOWING MIXED-LAYER CHARACTERISTICS*

G. W. BRINDLEY, *Mineral Science Building, The Pennsylvania State
University, State College, Pa.*

ABSTRACT

X-ray and electron diffraction studies confirm that stevensite belongs to the montmorillonite group of minerals. The basal spacings are variable and show a poorly developed sequence of non-integral character. Some specimens show a long spacing of about 24–25 Å. Organic liquid complexes also show a poorly developed sequence of basal reflections and occasionally a long spacing of about 26 Å. Heat-treatment up to 400° C. reduces the basal spacing to about 9.6 Å. It is suggested that the mineral may have a mixed-layer sequence consisting normally of about 10 and 14 Å units, the latter showing swelling and shrinking characteristics; it may be described as a talc-saponite interlayered mineral. Electron micrographs are reproduced.

INTRODUCTION

Stevensite has recently been examined by Faust and Murata (1953) who have shown that it belongs to the montmorillonite group. The swelling characteristics which they report, namely a 001 spacing of 15.1 Å after treatment with ethylene glycol and “no easily detectable swelling” when a fragment is dropped in water, together with an abnormally low cation-exchange capacity, suggested to the writer that the mineral might have anomalous features as compared with others in this group. Dr. G. Switzer of the U. S. National Museum kindly supplied a specimen of stevensite (U.S.N.M. R 4719) from Springfield, New Jersey, a source from which Faust and Murata also obtained material. The mineral has been examined by x-ray diffraction using a Norelco Straumanis-type camera of diameter 11.46 cm. and Geiger counter recording spectrometers (General Electric XRD-3 and North American Philips high-angle instrument), and by electron diffraction and electron microscopy using RCA instruments. The swelling of the mineral in a series of organic liquids has been measured.

X-RAY AND ELECTRON DIFFRACTION ANALYSIS

X-ray powder diagrams taken with specimens prepared in a variety of ways show a clearly defined pattern of the montmorillonite type, (Fig. 1, *a* and *b*). Faust and Murata indexed the diagram “on the basis of the work of Faust (1951) on the related mineral sauconite” in which a monoclinic formula was used. This does not conform with current views of diffraction by montmorillonite and similar minerals. The broadly

* Contribution No. 53-61 from the College of Mineral Industries.

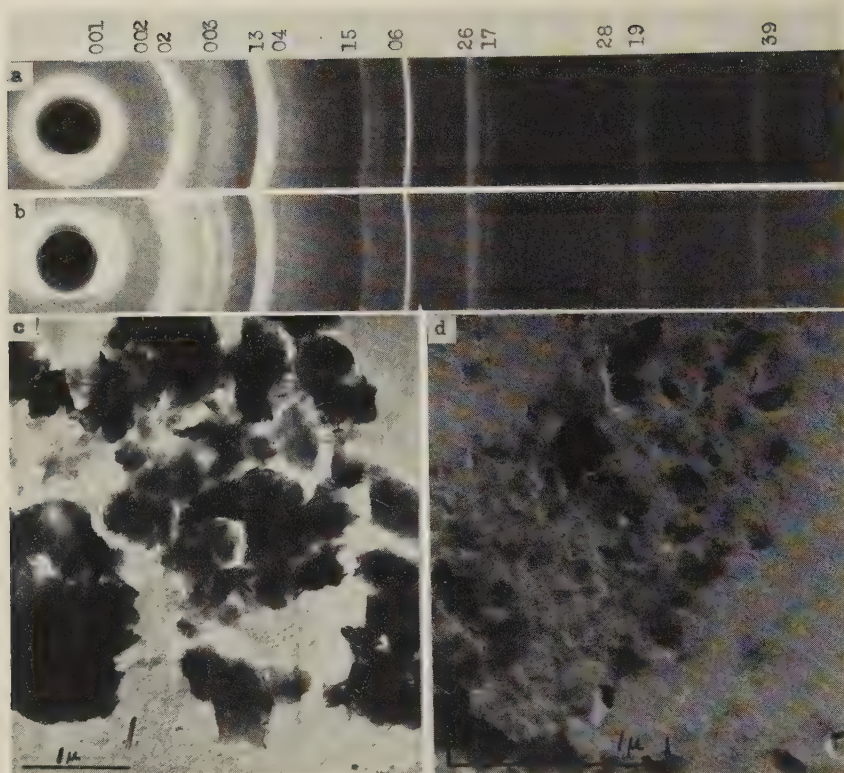


FIG. 1. (a) and (b)—X-ray powder diagrams of air-dry stevensite, with 00*l* and *hk* indices of the reflections. (a)—Random layer sequence, (b)—partial segregation of 10 and 14 Å layers. (c) and (d)—Electron micrographs of platinum-shadowed stevensite.

spreading diffraction bands represent coherent scattering from single layers of the mineral and monoclinic parameters do not exist, (see Brindley 1951, Brindley and Méring, 1951). The low-angle terminations of the bands correspond closely with *hk*0 positions in reciprocal space and the corresponding *d* values can be calculated from the layer parameters *a* and *b* or, for hexagonal layers, from a single parameter *a* or *b*.

The results of the diffraction analysis are summarized in Table 1. The first column gives the indices of the reflections which are of types 00*l* and *hk*. The intensities are visually estimated and the x-ray values are for specimens with a minimum of preferential orientation. The 00*l* spacings are variable and at the best correspond only roughly with an integral series; a precise basal spacing cannot be given. In addition, many of the counter-spectrometer records shown an indication of a weak reflection at about 24–25 Å; see, for example, figure 2b for an orientated air-

TABLE 1. INDEXED POWDER DIAGRAM OF AIR-DRY STEVENSITE
(from Springfield, N. J.; U.S.N.M. R 4719)

X-ray data; filtered $\text{CuK}\alpha$ radiation, $\lambda = 1.542 \text{ \AA}$

Electron data; 50 kV electrons calibrated with MgO , $a = 4.213 \text{ \AA}$

Indices	Intensities		Spacings, d (\AA)			
	X-ray	Electron	X-ray	Electron	Calculated	Faust & Murata
—	—	—	24	—	—	—
~ 001	10+	—	11.2–12.4	—	—	14±
~ 002	2	—	4.89–4.96	—	—	—
02, 11	10	10+	4.54	4.53	4.56	4.55
~ 003	5	—	3.0–3.5	—	—	3.20
13, 20	9	10	2.618	2.64	2.635	2.63–2.53
04, 22	2	2	2.279	2.26	2.280	2.284
15, 24, 31	4	7	1.725	1.717	1.725	1.722
06, 33	9	10	1.520	1.514	1.520	1.526
26, 40	7	9	1.314	1.314	1.317	1.315
17, 35, 42	2	4	1.265	1.263	1.266	1.265
08, 44	—	1	—	1.139	1.140	—
28, 37, 51	1	2	1.047	1.043	1.046	—
19, 46, 53	3	5	0.994	0.989	0.995	0.990
0.10, 55	—	$\frac{1}{2}$	—	0.910	0.912	—
39, 60	3	5	0.879	0.877	0.878	0.879
57, 64, 1.11	—	$\frac{1}{2}$	—	0.815	0.819	—
0.12, 66	—	4	—	0.759	0.760	—
2.12, 59, 73	—	2	—	0.727	0.731	—
1.13, 68, 75	—	$\frac{1}{2}$	—	0.690	0.696	—
4.12, 80	—	1	—	0.653	0.658	—
3.13, 5.11, 82, 14.0	—		—		0.652	—

dry specimen sedimented on a glass plate. The hk spacings correspond to the low-angle terminations of the bands in all cases where there is a spreading of intensity towards higher angles. The calculated spacings are obtained from the formula,

$$(1/d)^2 = (3h^2 + k^2)/b^2$$

and the b parameter, 9.12 \AA , is derived from the sharp 06 reflection. With $\text{CuK}\alpha$ radiation the hk reflections can be measured down to 0.879 \AA . Electron diffraction diagrams taken by transmission through thin films mounted on collodion extend the range of measurements down to 0.652 \AA . The latter are calibrated by reference to MgO using the spacings determined by Swanson and Tatge (1953). The x-ray values are considered to be accurate to about 0.2% and the electron values to about 0.5%. The

agreement between the two sets of measurements and the calculated values is very close throughout. All hk reflections theoretically possible have been recorded. The index sum $(h+k)$ is always even in accordance with the centering of the layer unit. There is close agreement also with the experimental data of Faust and Murata which are listed in Table 1, but in the writer's opinion their indexing of the diagram in terms of monoclinic parameters is incorrect; they also list some indices with $(h+k)$ an odd number.

THE BASAL REFLECTIONS; EVIDENCE FOR A MIXED-LAYER STRUCTURE

The occurrence of a 24–25 Å reflection, taken in conjunction with the poorly developed and non-integral basal reflections suggests a mixed-layer structure containing layers of about 9.5–10 and 14–15 Å thickness. A partially regular alternation of two such layers would account for a weak reflection at about 24–25 Å. If integral sub-multiples of 9.5, 10, 14 and 15 Å units are set out as follows:

15.0	7.5	5.00	3.75	3.00	2.50		2.14
14.0	7.0	4.67	3.50	2.80		2.33	2.00
	10.0	5.00	3.33		2.50		2.00
	9.5	4.75	3.17			2.37	1.90

then an irregular or imperfectly regular alternation of the two components would be expected to give scattering maxima around 12 Å, 4.8–4.9 Å, 3.2–3.5 Å and 2.0–2.1 Å. The first three are in accordance with the observed results. The 4.8–4.9 Å line is sharp and constant from one specimen to another, while the 12 Å and 3.2–3.5 Å lines are broad, and variable (c.f. Figs. 1*a* and *b*).

Méring (1951) has discussed theoretically how partial order in a sequence of layers influences the diffraction effects. Partial order may occur as a tendency towards either segregation of the two components, or their regular alternation. Both tendencies have been observed with stevensite. Some specimens (see Fig. 1*b*) show the 11–12 Å line spreading outwards towards 10 and 14 Å and the 3.2–3.5 Å line almost splitting into two separate components with continuous scattering between them. This represents a tendency towards segregation of the components. More commonly there is no splitting of the 11–12 Å line nor of the 3.3 Å line which remains very broad. This, together with the occurrence of the 24–25 Å line, represents a tendency towards alternation of the two components (see Fig. 1*a*); the long spacing is shown only in spectrometer records).

It appears that stevensite is a rather variable material and contains layers of two kinds which show a tendency in some fragments to segregate, and in others to give a partial alternation. The question which has

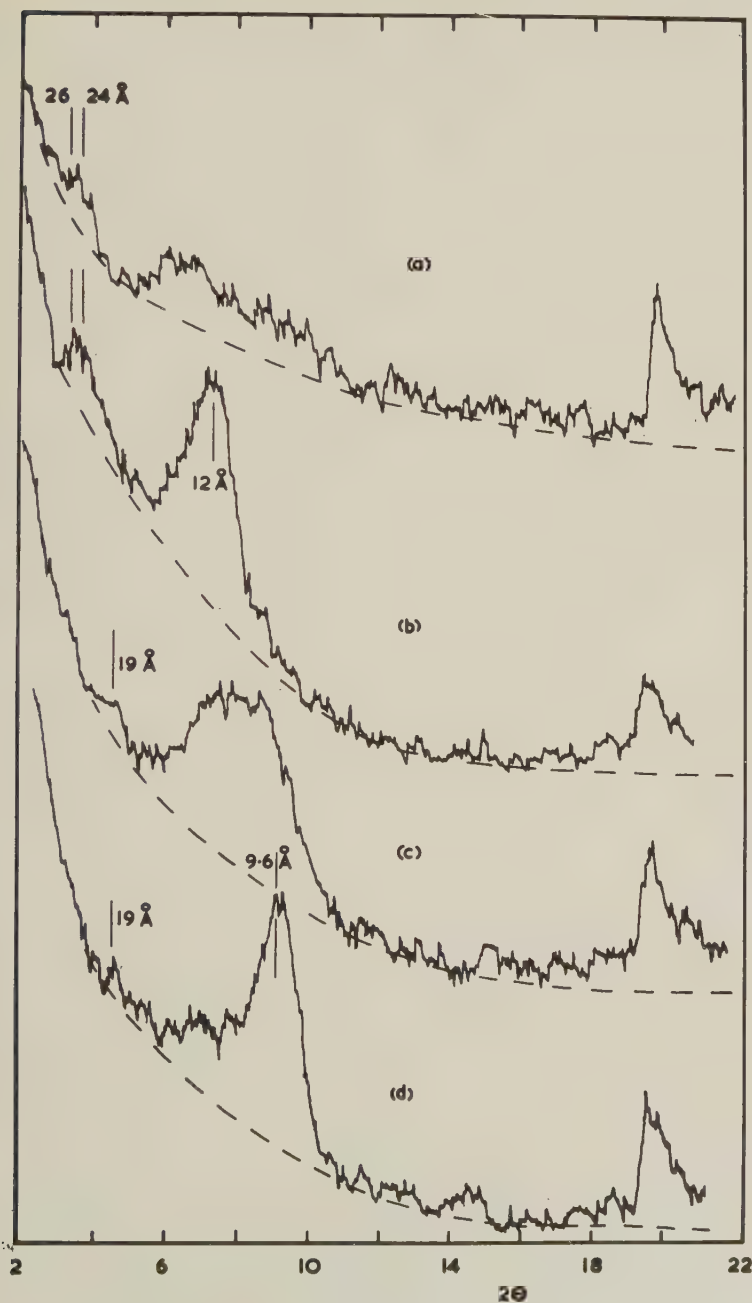


FIG. 2. Geiger counter spectrometer records for stevensite. (a) Water-wet material. (b) Air-dry material oriented on glass slide. (c) Air-dry material heated for 1 hr. at 105° C. and immediately x-rayed. (d) Material heated for 3 days at 400° C.

to be considered is whether the two kinds of layers are basically different, or whether they arise from a largely fortuitous difference in degree of hydration of the layers. Information bearing on this question may be obtained by studying the hydration and dehydration of the mineral and its organic complexes.

(a) *Hydration tests*: A specimen kept in water for 3 days and x -rayed in a moist condition with a counter spectrometer gave continuous scattering from 14–7.5 Å and clear evidence of a long spacing at about 25 Å (see Fig. 2a). Similar data were obtained with other water-wet specimens and there was no indication that wetting the mineral produced a more uniformly hydrated system.

(b) *Dehydration tests*: Low temperature heat-treatment up to 400° C. produced a collapse of the basal spacing to about 9.6 Å and the following reflections were observed: 9.6 Å, medium-strong and clearly defined, but with intensity spreading towards longer spacings (see Fig. 2d); 4.8 Å, weak and not fully resolved from the 4.5 Å band; 3.18 Å, medium-strong and clearly defined; 1.92 and 1.22 Å, both weak and broad. These reflections correspond to the orders 1, 2, 3, 5 and 8 from a basal spacing of 9.6 ± 0.1 Å. Traces of a long spacing of about 19 Å are found (see Figs. 2c and d) but the evidence is uncertain. It is clear that the 14–15 Å layers collapse in a similar manner to hydrated montmorillonite layers, and a more regular structure is produced. Any differences now remaining between the layers are too small to be detected with any degree of certainty.

Since montmorillonite-organic complexes normally give a well-ordered sequence of basal reflections, numerous attempts were made to expand the stevensite layers in a similar way. The results are described in the following section.

ORGANIC COMPLEXES OF STEVENSITE

The swelling of stevensite in a number of organic liquids, mainly dihydric alcohols, has been investigated with a Geiger counter spectrometer which easily records spacings to 30 Å. Oriented layers obtained by sedimentation and randomly oriented specimens have been used. The results of many tests show that the number, sharpness and regularity of the reflections are much inferior to those obtained with montmorillonite-organic complexes. A first order reflection at about 17–18 Å spacing is usually the only clearly defined basal reflection. A weak second order at about 8.5–9.5 Å often appears. Higher orders are weak and diffuse and cannot be reliably correlated with a particular basal spacing. Evidence is obtained occasionally of a longer spacing and one complex with glycerol showed a clearly defined spacing of 26 Å, but higher orders could not be detected.

TABLE 2. "FIRST" ORDER SPACINGS OF ORGANIC LIQUID COMPLEXES WITH STEVENSITE

Organic Complex	<i>d</i> (Å)
ethylene glycol	17.0
1.3 propane diol	18.2
1.4 butane diol	17.3
1.5 pentane diol	18.0
1.12 polyethylene diol	17.3
ethylene glycol mono-butyl ether	13.8
diethylene glycol	16.7
glycerol	17.7

The available evidence points to an irregular layer sequence of spacings of about 17 and 10 Å. The curves calculated by Brown and MacEwan (1951) for such a sequence having a predominance of 17 Å layers show a "first" order at about 17 Å or a little higher spacing, a "second" order at about 9 Å together with higher orders which cannot be reliably identified in the spectrometer traces.

The poorly developed sequence of basal reflections and the occasional appearance of a long spacing in the region of 26 Å constitute the main evidence for a mixed-layer structure from the organic complexes.

Table 2 records the "first" order spacings observed for a number of stevensite-organic complexes. The smaller expansion to 15 Å found by Faust and Murata is not confirmed.

ELECTRON MICROGRAPHS

Electron micrographs of stevensite are reproduced in Figs. 1*c* and 1*d*. The mineral was crushed and lightly ground in a mortar, dispersed in water and allowed to sediment; fine fractions about 1 μ and 0.1 μ in size on collodion films were examined before and after platinum shadowing. The appearance of the mineral is closely similar to that of many montmorillonites. The finest fraction, Fig. 1*d*, shows very thin plates with irregular outline. The 1 μ fraction, (Fig. 1*c*), consists largely of irregular aggregates, the edges of which appear to show curled fragments.

DISCUSSION

The diffraction data confirm and extend those given by Faust and Murata. The mineral is of the expanding layer type and has a *b* parameter of 9.12 Å which is in accordance with its trioctahedral composition (c.f. talc, *b*=9.10; hectorite, *b*=9.16, vermiculite, *b*=9.18–9.20).

The long spacing of about 24–25 Å from air-dry material and about

26 Å from organic complexes are consistent with an interlayering of 9.5–10 and 14–15 Å layers in the air-dry material and 9.5–10 and 17–18 Å layers in the organic complexes. Low temperature heat-treatment gives a basal spacing of about 9.6 Å which results from a collapse of the 14 Å layers. It appears that the mineral is composed of two kinds of layers, of which one is capable of expanding and collapsing like the layers in montmorillonite, and the other appears to remain stable at about 9.5–10 Å.

The question arises whether the presence of these two kinds of layers can be correlated with the low cation-exchange capacity reported by Faust and Murata. If the exchangeable cations are associated with only the swelling part of the mineral then the exchange capacity of the swelling part is correspondingly greater. It is not justifiable to claim this as support for the mixed-layer hypothesis since there is no a priori reason why the exchange capacity should not be as small as the value which is reported. The differential thermal analyses given by Faust and Murata provide no direct indication of the presence of two kinds of layers, but it may be significant that, in their comparison of stevensite with the magnesian montmorillonite, saponite, they find the low temperature endotherm associated with the removal of interlayer water is only about half as large for stevensite as for saponite, the weights of the samples being very similar. This result is consistent with there being fewer hydrated layers in stevensite, but this evidence must be accepted cautiously since the hydration of montmorillonite-type minerals depends considerably on the humidity of the atmosphere and the nature of the exchange cations.

The hypothesis that stevensite consists of swelling and non-swelling or hydrated and non-hydrated layers may be linked with the suggestion, discussed by Faust and Murata, that it "might be a hydrated form of talc." Now talc itself has a basal spacing of about 9.4 Å. Stevensite, when dehydrated, gives a spacing of 9.6 ± 0.1 Å, which could be interpreted as an average of 9.4 Å and a value suitably larger than 9.6 Å depending on the proportions of the two components. The basal spacings of air-dry stevensite may also be interpreted in terms of talc-like layers of spacing 9.4 Å and hydrated layers with a spacing of 14–15 Å. The chemical analyses of stevensite given by Faust and Murata show very little K_2O and the CaO , also small, is largely exchangeable. There is no chemical evidence, therefore, to suggest that the non-swelling layers are mica-like with a spacing of about 10 Å.

The combined evidence of the present work and that of Faust and Murata is that stevensite consists of talc-like layers, some of which (like those in normal talc) do not swell in water and in organic liquids, and others (due to an octahedral ion deficiency as pointed out by Faust and Murata) have exchangeable cations and swell like montmorillonite (or

saponite) layers. Since Mg occupies most of the octahedral positions, it seems reasonable to describe the mineral as a talc-saponite interlayered mineral; this comes close to the earlier description of it as a hydrated talc.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Dr. G. Switzer of the U. S. National Museum for the specimen of stevensite used in this work and to Mr. J. Comer, of the Mineral Constitution Laboratories, The Pennsylvania State University, for taking the electron micrographs and assisting with the electron diffraction study.

REFERENCES

- BRINDLEY, G. W. (1951), *X-ray identification and crystal structures of clay minerals*: (Mineralogical Society, London). See especially Chs. IV and XII.
- BRINDLEY, G. W., AND MÉRING, J. (1951), Diffraction des rayons *X* par les structures en couches désordonnées I: *Acta Cryst.*, **4**, 441-447.
- BROWN, G., AND MACEWAN, D. M. C. (1951), In *X-ray identification and crystal structures of clay minerals*: (Mineralogical Society, London)—Ch. XI.
- FAUST, G. T. (1951), Thermal analysis and *x-ray* studies of sauconite and of some zinc minerals of the same paragenetic association: *Am. Mineral.*, **36**, 795-822.
- FAUST, G. T., AND MURATA, K. J. (1953), Stevensite, redefined as a member of the montmorillonite group: *Am. Mineral.*, **38**, 973-987.
- MÉRING, J. (1951), Les reflexions des rayons *X* par les minéraux argileux interstratifiés: *Trans. Fourth Inter. Congress Soil Science, Amsterdam*, **3**, 20-26.
- SWANSON, H. E., AND TATGE, E. (1953), Standard *x-ray* diffraction powder patterns. **1**, 37-38. (*Nat. Bur. Stds.*, Washington.)

Manuscript received April 7, 1954.

CRYSTALLOGRAPHY OF JADEITE CRYSTALS FROM NEAR CLOVERDALE, CALIFORNIA

C. W. WOLFE, *Boston University, Boston, Massachusetts.*

ABSTRACT

Good crystals of jadeite, a few doubly terminated, have been discovered by Dr. John Peoples of Petaluma, California, along the Russian River near Cloverdale, California. *Optical data:* $\alpha = 1.640$, $\beta = 1.645$, $\gamma = 1.652$, all ± 0.003 ; biaxial positive; $2V = 67^\circ$; elongation positive; nonpleochroic; extinction angle $Z \wedge c = 40^\circ$; $Y = b$. *Crystallographic data:* $a:b:c = 1.1026:1:0.6110$; $\beta = 107^\circ 38\frac{1}{2}'$; Forms: $b\{010\}$, $a\{100\}$, $i\{130\}$, $m\{110\}$, $y\{101\}$, $u\{111\}$, $s\{\bar{1}11\}$, $\Delta\{\bar{3}11\}$. Twin index, 1; obliquity, $1^\circ 34'$. *X-ray data:* $a_0 = 9.48$, $b_0 = 8.59$, $c_0 = 5.23$ KX; $\beta = 107^\circ 26'$; $a_0:b_0:c_0 = 1.104:1:0.609$; space group $C 2/c$. *Chemical analysis:* indicates composition of 94% jadeite, 6% diopside.

INTRODUCTION

Good crystals of jadeite are rarities. It was with considerable pleasure therefore, that the author received a few crystals of the mineral from Dr. John W. Peoples of Petaluma, California, through the good services of Dr. Leland Wyman of Boston University. The goniometric, optical, and x-ray investigation which followed indicated that the material was indeed jadeite, and Dr. Peoples was contacted in the hope of getting more and better crystals. He graciously put the best of his material at the author's disposal, and the present paper results from a study of the crystals and matrix specimens which he supplied.

MORPHOLOGY

Goniometric examination of approximately 30 crystals yielded the elements and forms listed in the following angle table.

JADEITE. MONOCLINIC; PRISMATIC-2/*m*

$$a:b:c = 1.1026:1:0.6110; \beta = 107^\circ 38\frac{1}{2}'; p_0:q_0:r_0 = 0.5541:0.5823:1$$

$$r_2:p_2:q_2 = 1.7174:0.9517:1; \mu = 72^\circ 21\frac{1}{2}'; p_0' = 0.5815, q_0' = 0.6110, x_0' = 0.3181$$

Forms:	ϕ	ρ	ϕ_2	ρ_2	<i>C</i>	<i>A</i>
<i>b</i> 010	0°00'	90°00'	—	0°00'	90°00'	90°00'
<i>a</i> 100	90 00	90 00	72°21'	90 00	72 21	0 00
<i>i</i> 130	17 36	90 00	0 00	17 36	84 44½	72 24
<i>m</i> 110	43 35	90 00	0 00	43 35	77 56	46 25
<i>y</i> 101	90 00	41 58½	24 19½	90 00	24 19½	48 01½
<i>u</i> 111	55 49	47 24	48 01½	65 34	33 56½	52 29½
<i>s</i> $\bar{1}11$	—23 19	33 38½	104 45½	59 25½	43 22½	102 40
Δ $\bar{3}11$	—66 48½	57 12	144 58	70 40½	73 37½	140 35½

Description of Forms. The two dominant forms on most of the crystals were the third order prism $\{110\}$ and the fourth order prism $\{111\}$. On one crystal habit $\{100\}$ was the principal form, but this was observed on only five crystals. On the crystals of the first habit minute additional forms were observed in fair position, as is summarized in the tabulation below. The crystals which were tabular on $\{100\}$ are not included in the tabulation because of the bad quality of their reflections.

MEASURED AND CALCULATED ANGLES FOR JADEITE FORMS ON 7 BEST CRYSTALS

Form	Range in Size*	Range in Qual.*	No. Xls.	No. Times	Meas. ϕ Range	Meas. ρ Range	Calc. ϕ	Calc. ρ
010	3-4	4-5	4	5	0°00'–8°08'	90°00'	0°00'	90°00'
100	2-4	3-5	4	4	87 01–93 17	90 00	90 00	90 00
130	4	5	1	1	17 42	90 00	17 46	90 00
110	1-2	3-4	7	23	38 34–44 54	90 00	43 35	90 00
101	5	5	2	2	90 20	41 43	90 00	41 58½
111	2-4	1-4	7	14	55 36–56 54	47 06–47 26	55 49	47 24
$\bar{1}11$	5	5	1	1	–30 18	32 30	–23 19	33 38½
$\bar{3}11$	4	5	1	1	–71 00	55 30	–66 48½	57 12
Summary of best weighted values								
					ϕ	ρ		
				110	43°35'	90°00'		
				111	55 49	47 24		

* Size is graduated from (1) largest to (5) smallest; quality of signal is graduated from (1) excellent to (5) very bad.

Choice of unit. It may be noted from the elements that x_0' , 0.3181, is greater than $p_0'/2$, 0.2907. This means the convention has been disregarded that the pole of (001) should be that node in the zone [010] which is closest to the center of the projection when the axis of rotation is [001]. Two reasons for this choice follow. The only important terminal form receives the indices of $\{111\}$ when the third pinacoid (001) is chosen as was done here. If the node of the zone [010] closest to the center of projection was chosen as the base, the indices of the only important terminal form would be $\{211\}$. Therefore, from the viewpoint of simplicity of indices the chosen orientation is to be preferred. A second reason for this choice derives from the designation of the lattice mode which results. Before x-ray work was done it was decided that the two choices indicated

that the lattice mode would be *C*-centered in the chosen orientation and *I*-centered in the other orientation. Since *C*-centering is conventionally chosen, it was felt even more strongly that the chosen orientation was the desirable one. As will appear later, x-ray examination of single crystals demonstrated that this view of the lattice mode is correct.

Calculation of elements. Since the calculation of the elements for jadeite involves a procedure which is not too common, it may be desirable to develop the method here. The only satisfactory terminal form for calculation purposes was the fourth order prism $\{111\}$. Φ and ρ were determined with fair precision for this form on several crystals. The best average values are

$$\Phi_{111} = 55^\circ 49'; \quad \rho_{111} = 47^\circ 24'$$

$$x' \text{ coordinate on gnomonic projection} = \sin \phi \tan \rho = 0.8996 \quad (1)$$

$$y' \text{ coordinate on gnomonic projection} = \cos \phi \tan \rho = 0.6110 = q_0' = c \quad (2)$$

but:

$$x'_{111} = x_0' \text{ (the } x' \text{ coordinate of the base, which does not exist in these crystals)} + p_0'. \quad (3)$$

The determination of p_0' and x_0' from the x' value of $\{111\}$ is possible if a good Φ value is known for an $\{hk0\}$ form. In this case the Φ value for $\{110\}$ was dependable.

$$\Phi_{110} = 43^\circ 35'.$$

Since the poles of $\{110\}$ lie on the zero layer line of the reciprocal lattice when the *c*-axis is vertical while $\{111\}$ lies on the gnomonic representation of the first layer line, the plotted pole of (110) does not pass through the pole of (001) but through the point (000) on the zero layer.

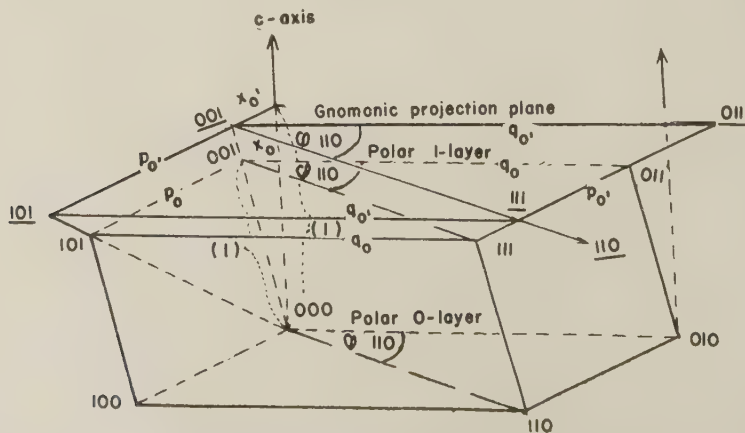


FIG. 1. Relation of (110) on 0-layer of polar lattice to (111) of 1-layer of polar lattice and (111) of the gnomonic projection plane.

If we imagine the pole of (001) to be shifted down to the origin (000), or vice versa, the directions to the faces of the form {110} would pass through the nodes of {111}, for they would be coincident. (Fig. 1). Thus we see that the

$$\tan \phi_{110} = p_0'/q_0' = p_0/q_0. \quad (4)$$

We have the ϕ of {110}, and we have q_0' (formula (2)). Thus, we have $p_0' = 0.5815$. Substituting in formula (3):

$$0.8996 = x_0' + 0.5815; \quad x_0' = 0.3181.$$

With x_0' , p_0' , and q_0' known, the calculation of polar and linear elements follows the usual pattern.

COMPARISON OF JADEITE ELEMENTS WITH THOSE OF OTHER PYROXENES

The following tabulation gives the elements of jadeite and of other pyroxenes for comparison. The values for the pyroxenes are excerpted from Dana (1892).

	<i>a</i>	<i>b</i>	<i>c</i>	β
Jadeite (Wolfe)	1.1026	1	0.6110	107°38½'
Jadeite (Penfield in Kunz)	1.103		0.613	107 44½
Russian and others (average)	1.0931		0.5895	105 48½
Diopside	1.0913–1.0922		0.5843–0.5895	105 25–105°51'
Augite (dark green)	1.0955		0.5904	105 46
Augite (yellow)	1.0921		0.5893	105 50
Acmite	1.0996		0.6012	105 49
Spodumene	1.1238		0.6355	110 20

It is to be noted that the *c* value for jadeite is closest to that of the NaFe pyroxene acmite, while the *a* value corresponds to the values of all listed pyroxenes except spodumene. The values for jadeite determined by Penfield (1906) are amazingly close to those of the present author. The crystals examined in this work are presumably of better quality than those possessed by Penfield. My values were determined before the record of Penfield's work was examined, and although the new values are very close to his, the new values for *c* and for β are probably preferable because of the better quality of the crystals and because a chemical analysis of the California crystals (which follows) indicates the purity of the material as jadeite.

The author was unable to examine the original work on jadeite by Kunz in which the crystallographic description was given by Penfield (Pt. 3-Jade as a mineral; p. 78). A transcribed quotation from that work

reads: "Specimen 51, said to be from Tibet, yielded two measurable crystals, each about 2 mm. long and 0.5 mm. across and terminated on one end. Colorless with vitreous luster. Forms: $\{100\}$, $\{110\}$, $n \{130\}$, $s \{\bar{1}11\}$."

The zone $[001]$ of most of the California crystals was striated, and a series of weak reflections in addition to the strong ones from $\{110\}$ could be picked up from line faces in the zone. The only weak reflection which was indexed was $\{130\}$, which is in agreement with Penfield's description. Since Penfield arrived at almost identical elements to those of this paper the indexing of his s plane as $\{\bar{1}11\}$ is proper although his one terminal

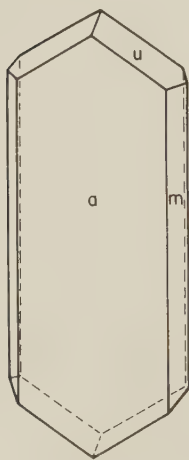


FIG. 2. Jadeite. Habit of first generation crystals.

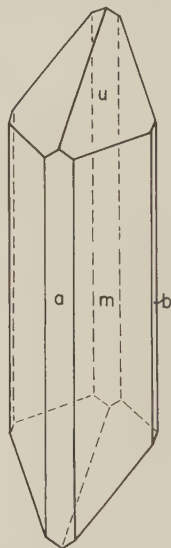


FIG. 3. Jadeite. Habit of Second generation crystals.

form was observed but once on my seven best crystals. My dominant terminal form is $u \{111\}$, not $s \{\bar{1}11\}$.

Crystal habit. Two distinctly different habits were observed, Figs. 2 and 3. Figure 2 represents the rather platy rectangular habit which is characteristic of crystals formed during the early stages of crystallization. Figure 3 pictures the elongated prismatic crystals which formed during the last stages of crystallization. The first or front pinacoid $\{100\}$ is the dominant form in habit 1, while in habit 2 $\{100\}$ is very much reduced in size or absent, and $\{110\}$ becomes dominant. Doubly terminated crystals were very rare but were noted for each habit.

Twinning. Twinning on $\{100\}$ is extremely common amongst the py-

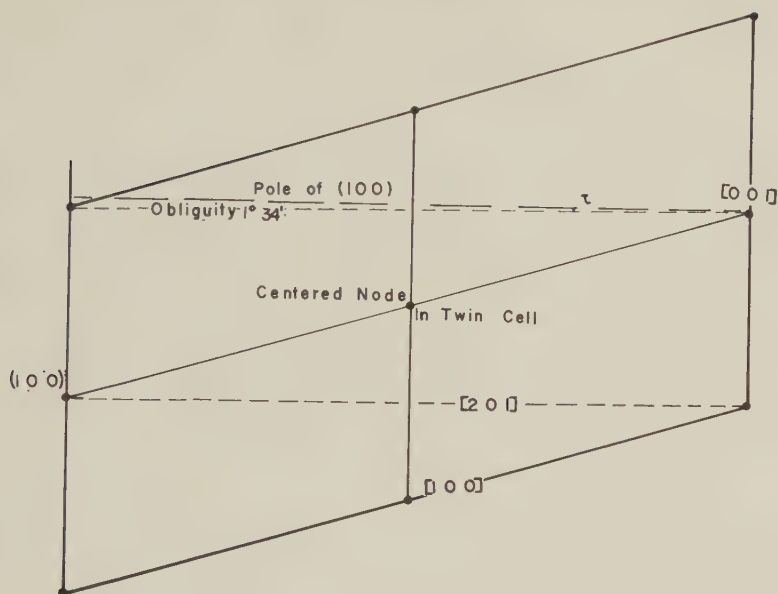


FIG. 4. Geometry of twinning in jadeite.

roxenes. From Fig. 4 it will be seen that the lattice row $[201]$ in the jadeite lattice is almost, but not exactly perpendicular to the front pinacoid (the twin plane) and, likewise, to the c axis $[001]$. The deviation from normality is the *obliquity of the twin*, according to the Friedel (1926) approach. Since this deviation is $90^\circ 00'$ minus the angle τ between $[001]$ and $[201]$, the calculation of the obliquity is very simple in this case, using the formula:

$$\cos \tau = c^2 + ca(w_1u_2) \cos \beta / T_{u_1v_1w_1} \cdot T_{u_2v_2w_2}$$

where $[001] = u_1v_1w_1$; $[201] = u_2v_2w_2$; a, b, c, β = the linear elements; $T_{u_1v_1w_1}$ = the periodicity along $[001]$; and $T_{u_2v_2w_2}$ = the periodicity along $[201]$.

If we use the rounded elements for augite of Rath (Dana, 1892),

$$a:b:c = 1.0921:1:0.5893; \quad \beta = 105^\circ 50',$$

we get an obliquity of $10' 51''$, which is an exceedingly low value. Since there is a node at the center of the multiple twin cell, the face-centered twin lattice repeats all of the nodes of the simple lattice, and the index of the twin is thus one (1). The low index of the twin coupled with the exceedingly low obliquity makes twinning on $\{100\}$ highly expectable, according to the Friedel approach. It should also be pointed out that the complimentary twin law of twinning by a rotation of $180^\circ 00'$ about $[201]$ is likewise expectable.

If we use the jadeite elements determined by the author, the obliquity of this twinning by pseudo-reticular merohedry is considerably greater: $1^{\circ} 34'$. It is interesting here to mention a rather simple method of checking the calculation of the obliquity. It is apparent that the pole of the lattice row $[201]$ must lie on the zone plane of the $\{h0l\}$ forms and must also be $90^{\circ} 00'$ from $(\bar{1}02)$. The ρ angle of $(\bar{1}02)$ is readily calculated from the projection elements (which were the fundamental elements from which the linear elements were obtained). This value is $1^{\circ} 34'$ with a ϕ value of $+90^{\circ} 00'$. The pole of $[201]$, therefore, lies in the southern hemisphere of projection and an angular distance of $1^{\circ} 34'$ from the pole of (100) , and this angle defines the obliquity, as was indicated above. It should be pointed out that the linear elements are rounded values obtained from the projection elements; and if the logarithmic values obtained before rounding had not been used, the value of $1^{\circ} 34'$ would not have been reproduced in each case.

Although the index of the twinning in jadeite is 1 as was the case in augite, the obliquity is much greater, and twinning is not as expectable, from the geometrical viewpoint. The fact that I have not observed twinning, either optically or morphologically indicates that the geometrical approach to twinning is sound in this case, as it has been in most cases where applied. Wolfe (1953) states: "The physical chemical forces which are involved in the accretion of ions, atoms, or molecules to form crystals have been studied of late; but as yet good quantitative measurements are not available. Since we are not clear as to the nature and magnitude of these forces, we cannot ascertain the precise nature of the equilibrium conditions involved in the growth of a single crystal. Neither, then, can we know at present what variations in the physical-chemical environment would produce first one position of growth equilibrium and then another to develop a twin. We are constrained to approach the subject of twinning, then, from a geometrical view." In essence these are the thoughts of Friedel on the best approach now available to twinning.

X-RAY DATA

Single crystal runs were made on crystals of the platy habit and of the prismatic habit. In addition, since some of the prismatic type crystals were colorless along most of their length but were colored green on the tips, single crystal runs were made of the green tipped and the colorless portions of the same crystal. The pictures of the platy crystals gave rather broad spots, making accurate measurement impossible, but aside from this fact no significant difference could be found in the dimensions of the unit cells of the three types of crystal material.

Rotation about the c axis gave the following data:

$$\begin{aligned}c_0 &= 5.25 \text{ KX} \\d_{100} &= 9.04 \\b_0 &= 8.60\end{aligned}$$

Rotation about the b axis yielded:

$$\begin{aligned}d_{001} &= 4.99 \text{ KX} \\d_{100} &= 9.05 \\b_0 &= 8.58 \\d_{101} &= 5.06 \\\mu &= 72^\circ 34'\end{aligned}$$

We have taken as the best fundamental values for the unit cell:

$$a_0:b_0:c_0 = 9.48:8.59:5.23 = 1.104:1:0.609; \quad \beta = 107^\circ 26'$$

which compare favorably with our goniometric values:

$$a:b:c = 1.1026:1:0.6110; \quad \beta 107^\circ 38\frac{1}{2}'.$$

Dr. Hatten S. Yoder, Jr. (1950) calculated the principal periodicities for jadeite from powder pictures, assuming that the elements of Penfield, given earlier in this paper, were correct. His values in Ångströms are:

$$a_0 = 9.45; \quad b_0 = 8.57; \quad c_0 = 5.25,$$

which is in good agreement.

There can be no doubt that the crystal class for jadeite is prismatic $2/m$. The 2-fold axis and symmetry plane are seen on many of the crystals. In addition a glide plane is indicated by the x -ray study, which confirms the existence of the symmetry plane. As was mentioned earlier, the lattice of jadeite is centered, and the orientation was chosen which makes the lattice centered on $\{001\}$, resulting in the presence of reflections which conform to the criteria: $\{hkl\}$ present when $h+k=2n$. The plane $\{010\}$ is a glide plane with a glide component of $c/2$, resulting in the occurrence of reflections of those $\{h0l\}$ planes for which l is even. The space group is, therefore, $C 2/c$, as was suggested by Yoder.

Impact of space group and elements on form development in jadeite. Friedel (1904) developed the thesis that the importance of a form is directly proportional to its reticular density or the spacing between planes. In this work he demonstrated that the lattice mode must be considered in determining spacings, as is well known now from x -ray studies. Donnay and Harker (1937) demonstrated that not only the lattice mode but also the effect of glide planes and screw axes must be considered in ascertaining the spacings within a particular crystal. It is interesting to remember that if the importance of a form in a particular crystal is directly proportional to its spacing as determined by the direct lattice

elements and the space group, the *importance of that form is inversely proportional to the periodicity from the origin of the reciprocal lattice to the node of the reciprocal lattice defined by the indices* (Wolfe, 1953). Since indices of faces (which is the customary method of designating a plane in the direct lattice) are coordinates within the reciprocal lattice of the normals to direct lattice planes, it would seem desirable to express the rule in terms of this reciprocal relationship. A particular periodicity in any three dimensional homogeneous network can be defined in terms of three coordinates (the indices in this case) in three different reference directions in that network or lattice. The three unit lengths used in defining the reciprocal lattice of morphological crystallography are p_0 , q_0 , and $r_0 = 1$ (a^* , b^* , c^* of x -ray crystallography). Any particular periodicity defined by the indices hkl may then be calculated by the following standard formula:

$$T_{hkl}^2 = h^2 p_0^2 + k^2 q_0^2 + l^2 + 2klq_0 \cos \lambda + 2lh p_0 \cos \mu + 2hk p_0 q_0 \cos \nu.$$

Since λ and ν are $90^\circ 00'$ in the monoclinic system, the formula is considerably simplified for the calculation of a reciprocal periodicity in this case.

Let us list those forms whose indices include no numbers higher than 2 and give the proper indices of those forms in view of the space group $C2/c$; give the periodicities of those forms, assuming $p_0 = 0.5541$, $q_0 = 0.5822$, $r_0 = 1$; a column will be devoted to the summation of indices, another to the theoretical importance of the form, and a final one to the observed importance of the form as nearly as it could be judged.

A perusal of the above tabulation demonstrates that the five best developed forms which were seen in good position on the jadeite crystals are included in the first eight forms with the shortest periodicities in the reciprocal lattice, and seven of the eight observed forms are included in the first eight of the forms listed according to increasing periodicities in the reciprocal lattice.

It will be seen that the only importance that can be ascribed to the rule of *simplest summation of indices* as a guide to the importance of forms is as follows. *The most important forms in any particular zone are those with the smallest summation of proper* (based on space group criteria) *indices*. The theoretical relative importance of forms with the same summation of indices in different zones can best be approached as was done above. It is obvious that this is but another approach to and demonstration of the Donnay-Harker principle. It is not necessary to demonstrate here that lattice spacings, in general, reflect physical bonding forces during the growth of a crystal, and that consequently the geometrical approach is an approximation to the physical approach which still eludes scientific precision.

Simplest indices	Proper indices	Summation of indices	Reciprocal periodicity	Form importance theoretical	Form importance actual
001	002	2	2		
010	020	2	1.16	4	4
100	200	2	1.11	2	2
110	110	2	0.80	1	1
120	240	6	2.58		
210	420	6	2.50		
130	130	4	1.83	8	5
101	202	4	2.56		6
102	204	6	4.46		
201	402	6	3.40		
$\bar{1}01$	$\bar{2}02$	4	1.97	10	
$\bar{1}02$	$\bar{2}04$	6	3.82		
$\bar{2}01$	$\bar{4}02$	6	2.50		
011	022	4	2.31		
012	024	6	4.17		
021	042	6	2.99		
111	111	3	1.41	5	3
112	112	4	2.31		
121	242	8	3.68		
211	422	8	3.63		
221	221	5	2.06		
$\bar{1}11$	$\bar{1}11$	3	1.14	3	7
$\bar{1}12$	$\bar{1}12$	4	1.91	9	
$\bar{1}21$	$\bar{2}42$	8	2.79		
$\bar{2}11$	$\bar{4}22$	8	2.72		
$\bar{2}21$	$\bar{2}21$	5	1.71	6	
$\bar{3}11$	$\bar{3}11$	5	1.76	7	8

PHYSICAL PROPERTIES

The following physical properties were noted for crystals of jadeite.

Hardness—6.

Cleavage—{110} good.

Color—first generation crystals are dull white; second generation crystals are colorless with sharp light to dark green tips.

Luster—dull lithic on first generation; vitreous on second generation.

Streak—colorless.

Specific gravity—3.245.

Optical properties

Biaxial positive.

 $\alpha = 1.640$, $\beta = 1.645$, $\gamma = 1.652$, all ± 0.003 . $2V = 67^\circ$.

Elongation-positive.

Non pleochroic. No abnormal interference colors.

No dispersion of the optic axes.

 $Y = b$; $Z \wedge c = 40^\circ$.

Comparison of optical properties.

Jadeite-Wolfe $\alpha = 1.640$, $\beta = 1.645$, $\gamma = 1.652$ Jadeite-Larsen and Berman $\alpha = 1.654$, $\beta = 1.659$, $\gamma = 1.667$ Diopside-Larsen and Berman $\alpha = 1.664$, $\beta = 1.671$, $\gamma = 1.694$

CHEMISTRY

Dr. George Switzer of the Smithsonian Institute learned of the occurrence of the jadeite crystals through Dr. Yoder of the Geophysical Laboratories and contacted Dr. Peoples for some material. Crystals were supplied for a chemical analysis. Unfortunately, the optical, goniometric, and x -ray studies of this paper were not made on this material, but it seems probable that all of Dr. People's material was homogeneous. Since Drs. Switzer and Fahey are working on the correlation of optical properties with chemical analyses of pyroxenes, they sent the sample to the University of Minnesota laboratory for analysis. Dr. Switzer has kindly released this analysis to make the treatment of the Cloverdale material as complete as possible. The analysis follows:

ANALYSIS OF JADEITE FROM NEAR CLOVERDALE, CALIFORNIA

	1	2	3	4	5	6	7	8
SiO ₂	61.66	61.74	8.215	59.20	7.88	59.20	59.44	55.48
Al ₂ O ₃	21.81	21.84	1.71	23.26	1.82	23.71	25.22	
TiO ₂	.05	.05						
Fe ₂ O ₃	.32	.32						
FeO	.24	.24	.03					
MnO	.05	.05						
MgO	.98	.98	.19	1.04	.21	1.12		18.62
CaO	1.38	1.38	.20	1.47	.21	1.55		25.90
Na ₂ O	12.27	12.29	1.58	13.08	1.69	14.42	15.34	
K ₂ O	.57	.57	.01					
H ₂ O(+)	.44	.44						
H ₂ O(-)	.10	.10						
Total	99.87	100.00				100.00	100.00	100.00

Columns: 1. Analysis of jadeite from near Cloverdale, California, by University of Minnesota laboratory; 2. Column 1, recalculated to 100%; 3. Molecules in unit cell assuming $V_0 = 406.3$, $d = 3.245$ (measured on Berman balance); 4. Approximate analysis

If we take the average content of the jadeite molecule to be 3.2 in column 3 and the average content of diopside to be 0.195, the percentage of jadeite molecules is 94 and of diopside, 6. It is clear that there should be 4 molecules of $\text{Ja}_{94}\text{Di}_6$ in the unit cell, but because of the probable admixed quartz, the analysis is high in SiO_2 and low in the other jadeite-diopside components. A fair calculated approximation of the quartz content is 6%. If we recalculate the analysis for its jadeite-diopside composition, eliminating 6% quartz, the adjusted analysis would appear as in column 4. This is, admittedly, an approximation (as is indicated by the deficiencies of theoretical molecular content shown in column 5), but it is certainly closer to the true analysis than that given in column 1.

OCCURRENCE

Dr. J. W. Peoples, the original discoverer of the jadeite from near Cloverdale, California, has kindly supplied the following information concerning the locale of the discovery. The source material is comprised of four boulders lying in the stream bed of the intermittent Russian River to the west of a point $2\frac{1}{4}$ miles north of the Sonoma County-Mendocino County line along the main north south route U. S. 101. There is a 60 foot drop from the road to the river at this place, and Dr. Peoples believes the boulders, which averaged about two feet in diameter, were rolled over the bank into the channel during road construction. There seems to be nothing of value left, as far as jadeite is concerned, at the locality. The source outcrops for the boulders have not been located as yet, but it is suspected that the boulders have not traveled far.

The jadeite occurs in light colored veinlets in a glaucophane rock. The veinlets vary in thickness from minute to as much as two inches across. No single veinlet is continuous for distances of much more than six times the thickness of the veinlet; the ends may pinch out or may end abruptly.

Serpentine seems to be the earliest mineral in the veinlets. Jadeite, platy on {100}, formed secondly and is probably the most abundant mineral in the veinlets. At the time the jadeite was forming the veinlets were apparently open spaces which the jadeite and calcite filled randomly without parallel orientation of adjacent crystals. Second generation jadeite, elongated parallel to [001] with predominant {110} grew upon the first jadeite, projecting into the remaining open space. In some cases, but not all, the tips of these second generation crystals are a very lovely transparent light emerald green in contrast with the water-clear lower

of jadeite from column 1, assuming a 6% contamination by water-clear quartz which was present in the jadeite matrix; 5. Molecules in unit cell of adjusted analysis listed in column 4; 6. Theoretical composition of $\text{Ja}_{94}\text{Di}_6$; 7. Theoretical composition of jadeite $\text{NaAl}(\text{SiO}_3)_2$; 8. Theoretical composition of diopside $\text{CaMg}(\text{SiO}_3)_2$.

parts of the prisms. Before this generation of jadeite was completely crystallized, water-clear pseudo cubic quartz crystals began to form concomitantly, and they appear as partially embedded, partially projecting crystals. A few very minute but choice crystals of water clear jadeite seem to have formed during the very last stages of this crystallization. The remaining open space in the veinlets was finally almost completely filled with calcite. Albite appears to be a late cavity filling in some cases. It is to be hoped that a more comprehensive and meaningful paragenesis can be worked out when and if the jadeite is found *in situ*.

ACKNOWLEDGMENTS

The author cannot help but express a most sincere admiration for amateur mineral collectors of the type represented by Dr. Peoples. Very few professionals would have the curiosity to examine boulders in a dry stream bed, and if they had, they probably would not have pursued that curiosity to the point of etching the specimens with acid to reveal the possibility of unusual crystals within. Very few professionals, with their concern for professional duties, would more than glance at the material, but Dr. Peoples realized that something different was present and continued persistently until an identification was finally made and the foregoing study was undertaken. He generously supplied material and information and has waited as patiently as possible for four years to see the results of the study.* I must also acknowledge that without the help of Dr. Wyman, another amateur mineralogist, the specimens would never have reached my door.

I should also like to express my appreciation for the chemical analysis which appears in this paper which was made available by Dr. George Switzer. Miss Daphne Riska was of considerable help in the determination of the physical properties.

REFERENCES

- DANA (1892), *System of Mineralogy*, John Wiley and Sons.
DONNAY, J. D. H., AND HARKER (1937), *Am. Mineral.*, **22**, 446.
FRIEDEL, GEORGES (1904), *Étude sur les groupements cristallins*, Saint Étienne, Paris.
(1926), *Leçons de cristallographie*, Burger and Ledrault, Paris.
PENFIELD (in KUNZ) (1900), *Investigations and studies in jade*, preliminary edition, Rahway, N. J., Mershon Company Press.
WOLFE, C. W. (1953), *Manual for geometrical crystallography*, Geopublishing Co., Watertown, Mass.
YODER, HATTEN S., JR. (1950), *Am. Jour. Sci.*, **248**, 225, 312. Consult this reference for an extended bibliography.

* Deceased September 22, 1954.

APPLICATION OF THE ELECTRON MICROSCOPE TO MINERALOGIC STUDIES*

EDWARD DWORNIK AND MALCOLM ROSS,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

A discussion of the use of the electron microscope in mineralogic studies and of sample preparation is followed by a series of electron photomicrographs showing the size, shape, and crystal habit of fine fractions of some uranium-bearing minerals from the Colorado Plateaus, lignite from North and South Dakota, phosphate minerals from Florida, and minerals synthesized in the laboratory. The information obtained from these photographs is useful in establishing paragenetic relations of associated minerals in uranium deposits, in supplementing mineralogic descriptions, and in guiding and checking separation techniques.

INTRODUCTION

This report is an outgrowth of mineralogic investigations conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission. Electron photomicrographs (Figs. 1-8) that were taken as part of these investigations reveal the size, shape and crystal habit of fine-grained minerals and sediments occurring in or associated with uranium deposits. These include sooty pitchblende, carnotite, tyuyamunite, and related vanadates of the Colorado Plateaus area; ultrafine fractions of lignite separates; leached-zone material and "slimes" from the Florida phosphate deposits; and schroeckingerite from Wyoming. Micrographs of synthetic minerals prepared in connection with studies of the torbernite and apatite groups are also shown. Photographs of surface features of polished and etched carbonate-fluorapatite sections, as revealed by the replica technique, suggest another approach to high-resolution study of compact minerals not easily disaggregated and dispersed for electron-microscope examination.

Electron micrographs of earthy hematite and wad, both showing a habit somewhat similar to that of pitchblende, and a mixture of descloizite and montmorillonite are also included.

Electron-diffraction patterns were made of many of the specimens examined in the electron microscope to build up a library of electron-diffraction patterns and to aid in the identification of these and other specimens.

The writers are indebted to fellow geologists who submitted material for electron-microscope examination, for their description and identification of samples, and for their aid in the interpretation of micrographs. Thanks are due to George Jansen for his assistance in the electron-

* Publication authorized by the Director, U. S. Geological Survey.

microscope laboratory in sample preparation and examination of his synthetic uranium minerals.

HISTORY

The use of the electron microscope as a tool in scientific research has become increasingly important during the past 12 years. Technical journals have carried many reports on its application to problems involving the study of materials in the submicroscopic and colloidal size range. Most of these studies have been in the fields of biology, chemistry, and metallurgy, but some applications have been made in mineralogy. The most significant application has been in the investigation of clay minerals that occur in the particle size range especially suitable for electron-microscope examination. Using the electron microscope the mineralogist can see individual clay particles that are irresolvable in the petrographic microscope. Humbert and Shaw (1941) presented a series of micrographs contrasting the crystalline plates of kaolinite with the apparently amorphous, fluffy particles of montmorillonite. Marshall, Humbert, and Caldwell (1942) presented results of their work on fractionation of beidellite, nontronite, magnesium bentonite, and attapulgite. These studies were followed by those of Kelley and Shaw (1942) on hydrodynamic considerations in relation to shape of particles, wherein electron micrographs afforded a direct measurement of two dimensions of particles, calculation of the third, and determination of the specific surface of various clay species.

Humbert (1942) reported on the particle shape and behavior of kaolinite- and montmorillonite group minerals and commercial deposits of fire clay and attapulgite. He suggested that the electron microscope be used as a rapid means of selecting raw materials for certain types of ceramic ware. Bates (1947) used the electron microscope in his investigation of slate to provide additional data on recrystallization of "illite" to larger plates or flakes and reorientation to parallel alignment, thus accounting for slaty cleavage. Ross and Hendricks (1945) in their work on minerals of the montmorillonite group used electron micrographs of hectorite, bentonite, and nontronite to show significant morphological differences in structurally similar minerals.

Perhaps the most comprehensive report on the application of the electron microscope to geologic research was made by Bates (1949), who illustrated specific applications and indicated new methods of approach to current geologic and mineralogic problems. A detailed study of the morphology of endellite and halloysite with the electron microscope was reported by Bates, Hildebrand, and Swineford (1950). Davis and others (1950) presented a collection of micrographs of clay minerals and related species.

DESCRIPTION OF INSTRUMENTS

The electron microscope used in these studies is the research type designed for study of particulate matter in the range of 0.001 to 10 microns. The range of magnification obtainable with the electron microscope is 1,000 to 22,800 times. Individual fields of view may be enlarged photographically to 100,000 times; this is generally accepted as the limit of useful magnification. For a more complete description of the electron microscope—its history, development, and modifications, discussion of electron lenses and image formation, and applications to scientific research—the reader is referred to an article by Zworykin and Hillier (1950).

Although the electron microscope may be used as a diffraction camera, a separate electron-diffraction unit is also used at the Geological Survey. This unit was designed specifically for work with powder mounts, single crystals, and reflection diffraction of polished and mineral surfaces. It may be used as a shadow microscope with magnifications from 500 to 1,000 times.

A third high-vacuum apparatus, the metal-evaporation unit, is used primarily to "shadow" specimens for electron micrography, and also to check experimentally the behavior of hydrated salts in high vacua, to prepare metallic standards for the calibration of the diffraction unit, and to deposit thin uniform metallic reflecting surfaces.

ADVANTAGES AND LIMITATIONS OF THE ELECTRON MICROSCOPE

The advantages and limitations of the electron microscope as applied to mineralogic investigations were evaluated by Bates (1949) and are considered briefly here. The chief advantage of the electron microscope is its increase in resolving power over the light microscope. The accepted value for the limit of resolution in the light microscope is 0.2 micron. A value of 0.001 micron or 10 angstrom units has been reached in high-resolution studies with the electron microscope, but in normal operation 0.01-micron particles can be readily resolved.

The biggest disadvantage of electron radiation is the very low penetrating power. No set value for maximum thickness can be given because the density of the material under examination must be considered. Thin platelets of micaceous minerals or asbestiform fibers are penetrable, whereas uranium minerals of approximately equal thickness appear opaque. To offset the lack of penetrating power of the electron beam the replica technique can be used for study of surface features of cleavage fragments, fracture surfaces, and etched polished sections.

Energy absorption of electrons by matter and resultant high temperatures lead to further difficulty in observing some mineral species. In-

tensity of the illumination must be kept at a minimum in order to avoid a change in the specimen, which would complicate interpretation of the resultant micrograph. The optical properties of minerals as determined in the petrographic microscope are, of course, not applicable when the minerals are imaged by electron radiation.

In general, then, the electron microscope can be expected to provide data on size, shape, and crystal habit of those minerals whose particle size is 0.001 to 10 microns. To a limited extent relative density and fusibility are indicated.

SAMPLE PREPARATION

The support for electron-microscope mounts is a standard-mesh, $\frac{1}{8}$ -inch diameter, stainless-steel or copper grid covered with a thin film of collodion. The film must be strong enough to support dispersed particles on its surfaces in a uniform plane and thin enough to avoid excessive scattering of transmitted electrons. These blank mounts are prepared by placing four or five drops of a 5-to-1 mixture of amyl acetate and collodion in the center of a large evaporating dish filled with distilled water. After the solvent evaporates, a thin film of collodion forms on the surface. The 200-mesh grids are placed on the film within an area the size of a glass microscope slide and picked up by cutting through the film in a downward motion and entrapping the grids between the film and a slide. After drying, these blanks are ready for sample preparation.

The specimen material may be dispersed on the surface by collecting it as dust or smoke; or it may be rolled on gently with a cotton swab. For a more uniform dispersion of fine particles, however, a wet method is generally used. The technique consists in disaggregating the sample in a mechanical mixer of the "blender" type in distilled water. After several minutes the suspension is poured into a tall vessel and allowed to settle until it assumes a slightly murky appearance. Droplets of the suspension are then pipetted from several depths in the vessel and transferred to the collodion-covered grids. After evaporation of the water the mounts are ready for examination in the microscope, or they may be placed in the metal evaporation unit for coating with some heavy metal such as chromium or uranium. This technique of coating with a metal in a high vacuum at a computed oblique angle enhances contrast in the specimen, gives a direct measure of the height of the particle, and—because of the relatively great depth (10–25 microns) of focus of the electron microscope—portrays the general shape of the particle.

In the study of compact and dense materials it is necessary to resort to a replica technique to ascertain fine structural detail. One of the quickest methods is to flood a polished, etched, or cleavage surface of a mineral

with a 7-to-1 amyl acetate collodion solution, and after evaporation of the solvent, to float the replica film on the surface of distilled water. This film may then be picked up by the 200-mesh grids in a method similar to that for preparing blank mounts. Because the film lacks contrast, it is metal-shadowed in the evaporation unit to emphasize depressions and ridges in the original surface. Although this is a negative replica technique, the true nature of the sample surface is revealed when the finished micrographs are viewed under appropriate incident light. A discussion and evaluation of other replica methods can be found in the manual edited by Drummond (1950).

Artifacts introduced into the sample during preparation make interpretation of finished micrographs difficult. Therefore great care must be taken to avoid contamination of the sample. The distilled water must be fresh to avoid bacterial development. Chemical dispersants and aerosols or wetting agents are rarely used. Whenever feasible certain samples are prepared by wet- and dry-mounting methods, although uniform dispersion is not generally attained by dry mounting. Rupturing of the film substrate, the effects of heating the mount in the evaporation unit, and the electron beam itself also give rise to artifacts that must be recognized as not inherent in the specimen.

Because sample preparation requires extreme caution, the trial of various techniques, and the necessity of reproducing the results before the characteristics of the material under examination are established, the electron microscopist must devote at least 60 per cent of his time to sample preparation.

CONCLUSIONS

In the study of lignite, phosphates, and uranium and vanadium minerals, data on the shape, particle size, and crystal habit of these materials in 10-micron range have been obtained and many more data are readily available. This information may prove helpful in supplementing mineralogic description, in guiding and checking separation techniques, and in establishing paragenetic relations of associated minerals in uranium deposits.

The clays and related species are particularly suitable for electron-microscope examination. Presence of attapulgite in the Florida phosphate deposits has been reported for the first time, and continuing *x*-ray spectrometer study of phosphorites by Z. S. Altschuler of the Geological Survey reveals that it is a major constituent in a zone of alteration at the top of the Hawthorn formation in the Land-Pebble field.

In connection with synthesis work, particle size and homogeneity of resultant products are readily determined by the electron microscope.

The application of the electron microscope to mineralogic studies has given other workers in related fields investigating similar materials a clearer insight into actual particle shape and size of some of the uranium-bearing minerals and associated sedimentary rocks.

Although the applications of the electron microscope to mineralogic investigation cited in this report are general in nature, they suggest that more exhaustive and detailed studies of the fine fractions of uranium-bearing minerals and sediments are warranted.

REFERENCES

- BATES, T. F. (1947), Investigation of the micaceous minerals in slate: *Am. Mineral.* **32**, 625-636.
- (1949), The electron microscope applied to geologic research: *New York Acad. Sci. Trans.*, ser. 2, **11**, no. 4, 100-107.
- BATES, T. F., HILDEBRAND, F. A., AND SWINEFORD, ADA (1950), Morphology and structure of endellite and halloysite: *Am. Mineral.*, **35**, 463-484.
- DAVIS, D. W., et al. (1950), Electron micrographs of reference clay minerals: *Am. Petroleum Inst. Preliminary Rept.* **6**, Research Project 49.
- DRUMMOND, D. G. (1950), The practice of electron microscopy: *Royal Micr. Soc. Jour.*, **70**, pt. 1, 56-73.
- HUMBERT, R. P. (1942), Particle shape and the behavior of clay as revealed by the electron microscope: *Am. Ceramic Soc. Bull.*, **21**, 260-263.
- HUMBERT, R. P., AND SHAW, B. T. (1941), Studies of clay particles with the electron microscope. I. Shapes of clay particles: *Soil Sci.*, **52**, 481-487.
- KELLEY, O. J., AND SHAW, B. T. (1942), Studies of clay particles with the electron microscope. III. Hydrodynamic considerations in relation to shape of particles: *Soil Sci. America Proc.*, **7**, 58-68.
- MARSHALL, C. E., HUMBERT, R. P., AND CALDWELL, O. G. (1942), Studies of clay particles with the electron microscope. II. The fractionation of beidellite, nontronite, magnesium bentonite, and attapulgite: *Soil Sci.*, **54**, 149-158.
- ROSS, C. S., AND HENDRICKS, S. B. (1945), Minerals of the montmorillonite group, their origin and relation to soils and clays: *U. S. Geol. Survey, Prof. Paper* **205-B**, 23-79.
- ZWORYKIN, V. I., AND HILLIER, J. (1950), *Microscopy: electron: Medical Physics*, **2**, 511-530.

Manuscript received April 7, 1954.

DESCRIPTION OF PLATES

In all the following illustrations the scale marker equals 1 micron or 0.001 mm. and represents both the magnification of the specimen in the original electron micrograph and photographic enlargement. Some of the specimens have been shadowed with chromium in the evaporation unit to enhance contrast and indicate particle thickness. Shadow areas appear light in these photomicrographs.

Identification of the material examined is based on petrographic or x-ray methods except where otherwise noted.

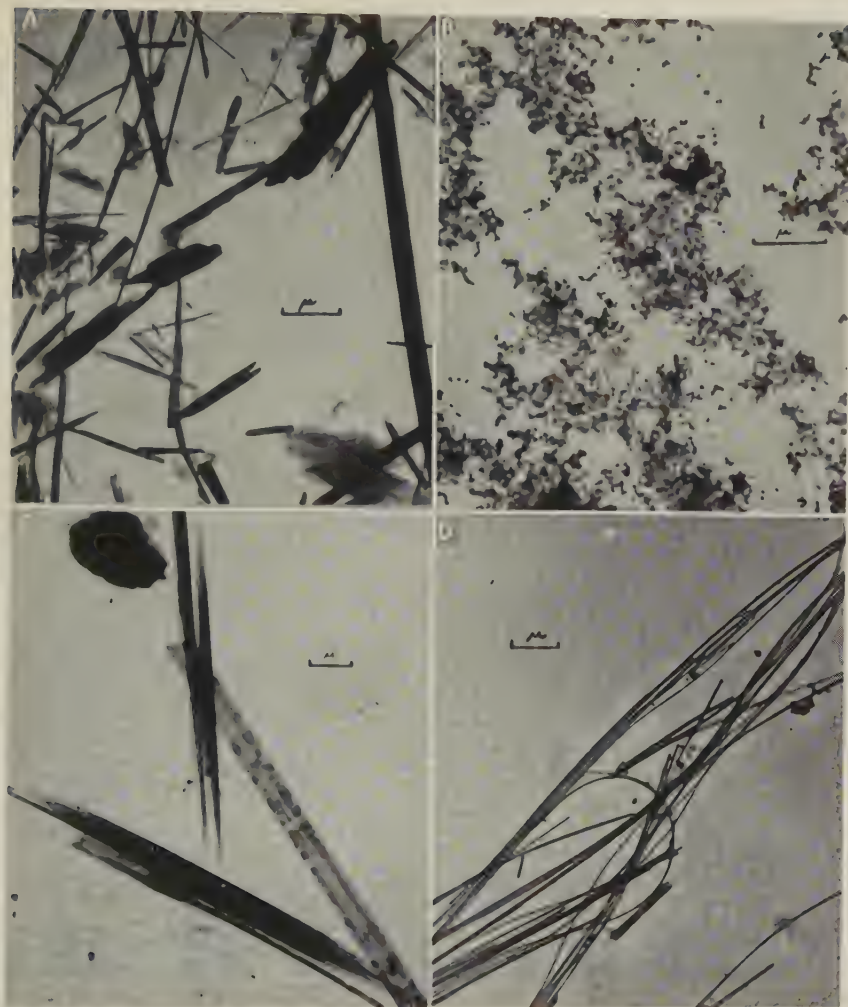


FIG. 1. (A) Iron vanadate, Jo Dandy mine, Montrose County, Colo. This mineral, as yet undescribed, shows a fibrous to lathlike habit different from the hewettite in *D* and also from the metahewettite of *C*, another related vanadate. Platy aggregates associated with the specimen probably belong to the montmorillonite group. (B) Schroëckingerite, Red Desert, Wyo. A well-dispersed mount showing particles of about 0.01 micron. The plate consists of material assumed to be recrystallized from solution. (C) Metahewettite, Matchless mine, Mesa County, Colo. A hydrated calcium vanadate with distinctly different morphology. The frayed hairlike terminations of the laths are characteristic of this mineral. Individual "hairs" are approximately a few hundred angstroms in thickness and are readily distinguishable from the hewettite fibers. The mottled effect on the lower lath is due to a moderately prolonged exposure to the beam. Further heating of the specimen leads to skeletalizing and fusion. Width of particles is 0.7 to 1 micron; maximum length is 15 microns. (D) Hewettite, Jo Dandy mine, Montrose County, Colo. This specimen shows a characteristic fibrous habit not unlike that of asbestiform serpentine. The fibers may be tubular in end section.

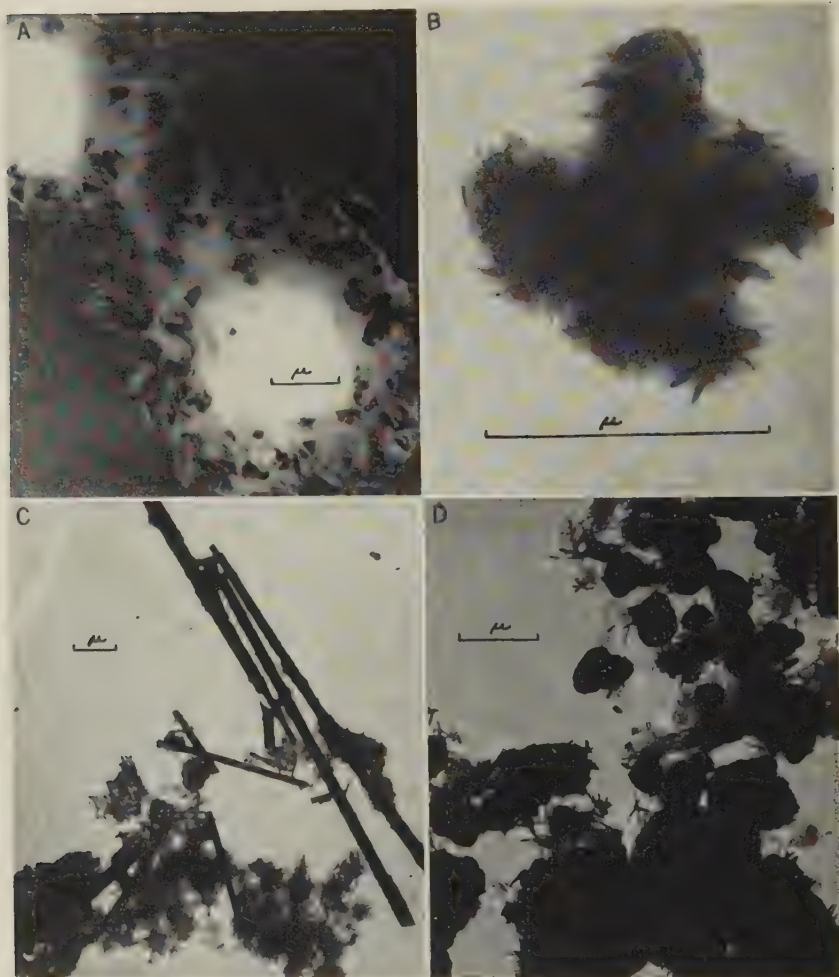


FIG. 2. (A) Sooty pitchblende (?) 300-foot level, Prospector mine, Piute County, Utah. This material shows a platy to lathlike character where individual particles are separated from the aggregate. Significance of the dark blebs associated with the particles has not been established. (B) Material presumed to be pitchblende from San Juan County, Utah. The width of the fibrous projection from the main mass of material is 100 to 200 Å. The density of the pitchblende is apparent from the relative opacity of the specimen to the electron beam. There is some suggestion of twisting and curling in the aggregate. (C) Wad (manganese oxides). This micrograph of supposedly amorphous material reveals the presence of two distinct morphological forms—the elongate laths and spherical clusters of short fibers. The individual needles comprising the aggregates are about 500 Å or 0.05 micron in thickness. The laths range in length up to 16 microns. (D) Hematite (earth). This material shows a habit similar to that of manganese oxides of the previous figure and sooty pitchblende. It is hoped that further study of apparently amorphous, natural, metal oxides will prove significant in mineralogic description of these minerals and related hydrates. Individual fibers are slightly coarser than those of the manganese oxides in C.

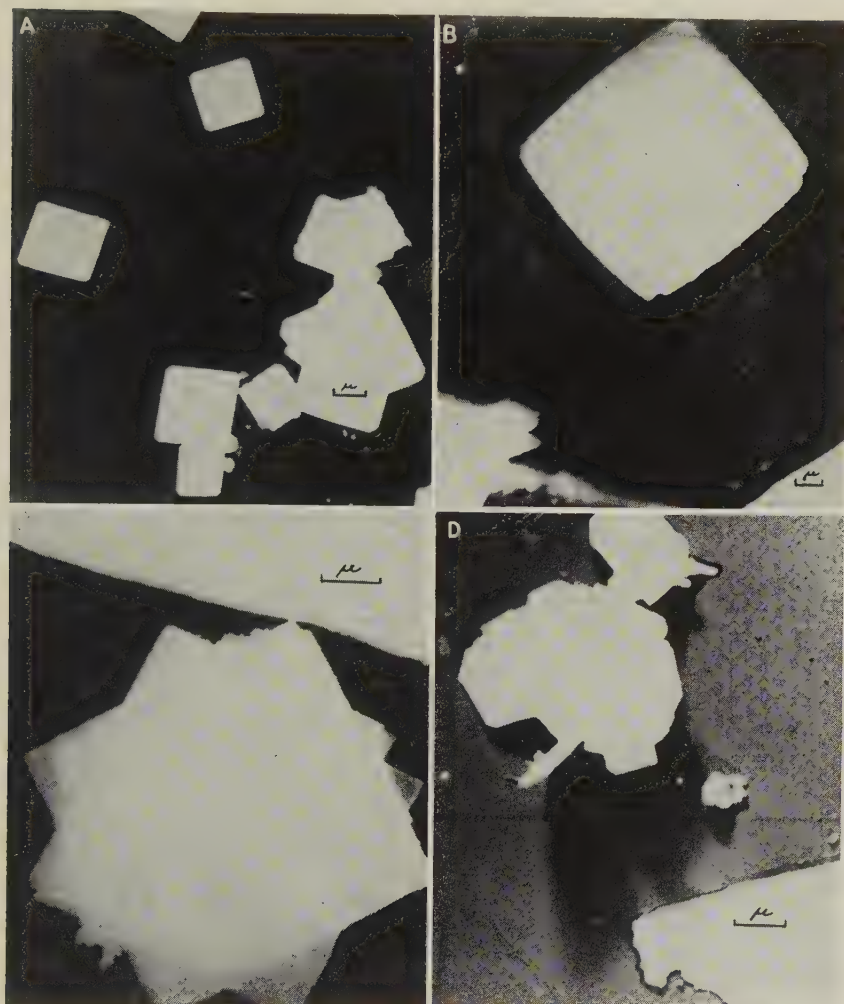


FIG. 3. (A) Synthetic uranocircite. This micrograph shows a well-crystallized synthetic product prepared by George Jansen of the Geological Survey. The mineral was identified by its x-ray diffraction pattern. Chromium shadowing shows that the material develops as thin tablets characteristic of the uranite group. Crystals vary in size from 1.5 to 3.5 microns along one edge. (B) Synthetic autunite. This mineral shows a square platy habit with particles as much as 8.5 microns along one edge. Its x-ray pattern is similar to that of autunite. Background irregularities are due to distortion of the film. (C) Synthetic parsonsite. Several square tablets of the synthetic product superimposed on one another. Crystals are about 5 microns along one edge. X-ray study shows a pattern similar to that of parsonsite with slightly larger spacings. (D) Synthetic bassettite. Electron-microscope examination shows a coarsely crystalline product essentially homogeneous with a pronounced development of prism faces. Size ranges from about 2 microns to particles greater than 15 microns. Product was identified by its x-ray diffraction pattern.

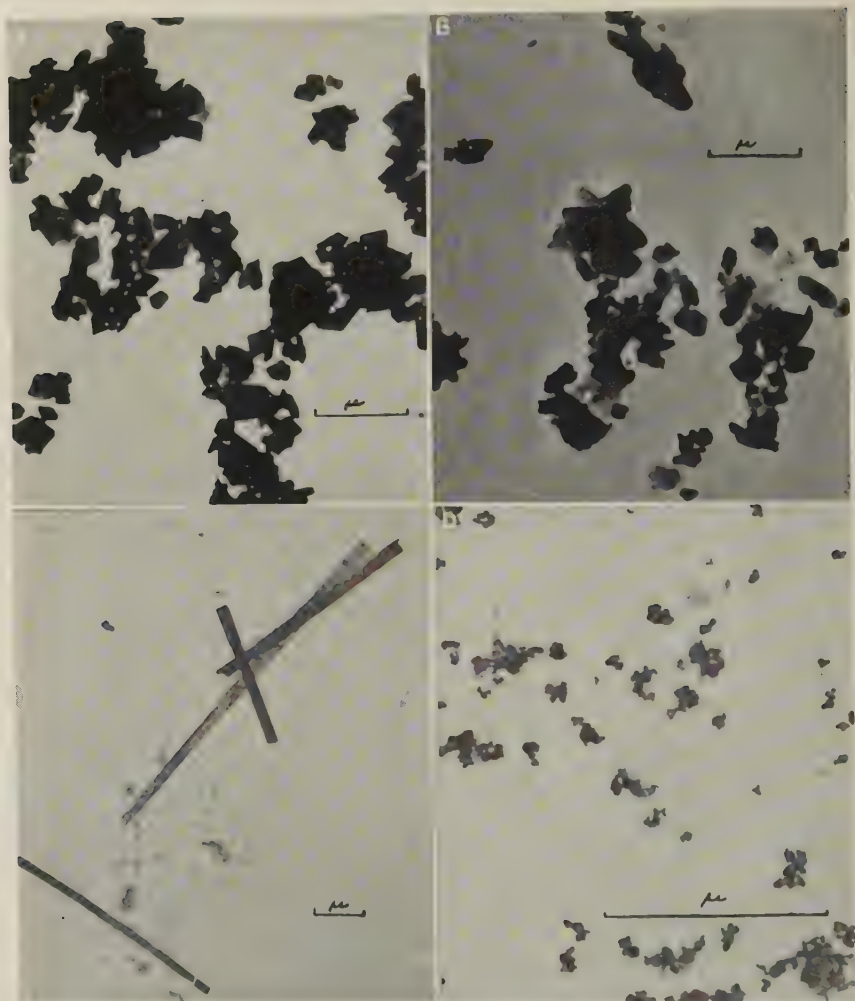


FIG. 4. (A) Synthetic carnotite. A micrograph showing a homogeneous product closely resembling natural carnotite in size and morphology. Compare with B. (B) Carnotite, Mine D, Yellow Bird group, Montrose County, Colo. Subhedral to euhedral overlapping plates of carnotite. Size of particles varies from 0.16 to 1.0 micron in longest dimension. The transparent platy material may be an admixed montmorillonite clay. (C) Synthetic α tricalcium phosphate prepared at Bureau of Plant Industries, U. S. Department of Agriculture. Material is lathlike in habit, approximately 0.25 micron in width, and as much as 5 microns long. (D) Synthetic hydroxylapatite, prepared at the Bureau of Plant Industries, U. S. Department of Agriculture. A homogeneous product examined at the Survey in connection with synthesis of apatite group members. Particle size 0.04 to 0.06 micron.

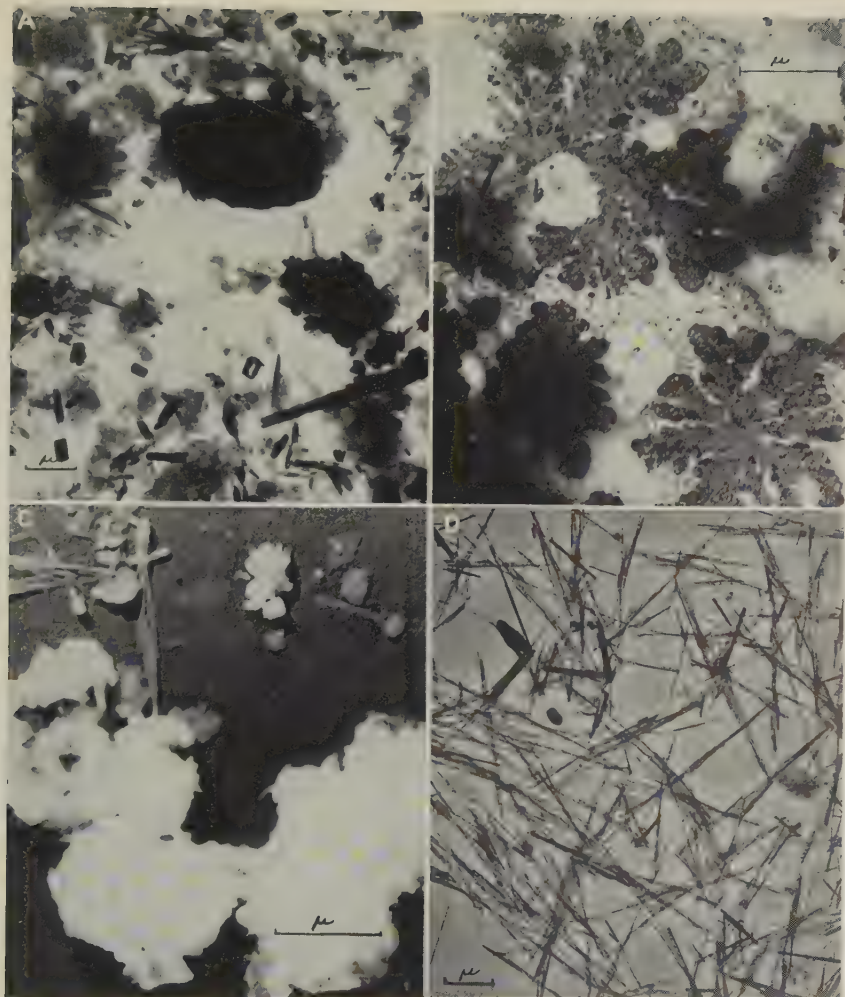


FIG. 5. (A) Fine fraction of phosphorite, Florida. The intimate mixture of distinct mineral species is indicated by the variety of crystal habit of the particles. Study of the picture reveals well-defined hexagons of kaolinite; lathlike, rod shaped, and fibrous particles; euhedral to subhedral rhombs and cubes; fluffy aggregates, presumably phosphorite; and remnants of organic structure. Particle size ranges from 0.03 to 3.5 microns. (B) Material from phosphorite fines, Florida. This plate illustrates the difficulty encountered in interpretation of micrographs. This material occurs sparingly in phosphorite fines. It may be an artifact introduced in sample preparation, a collapsing envelope of some minute organism or a recrystallized water-soluble mineral. Substances such as this are generally micrographed for future reference. (C) "Slimes" from phosphorite wastes, Florida. This material taken from the -150-mesh waste product of phosphate mining operations is, as expected, similar to the extremely fine material encountered in the examination of the phosphorite and leached-zone samples depicted in previous figures. (D) Attapulgite from leached-zone material, Florida. Initial examination of this material showed a surprising similarity to attapulgite. It was subsequently identified by E. B. Jaffe, U. S. Geological Survey, from its electron-diffraction pattern as attapulgite and marks a new occurrence of the mineral already reported from Attapulgus County, Ga., and Quincy, Fla. The more opaque lathlike particles may be wavellite or pseudowavellite.

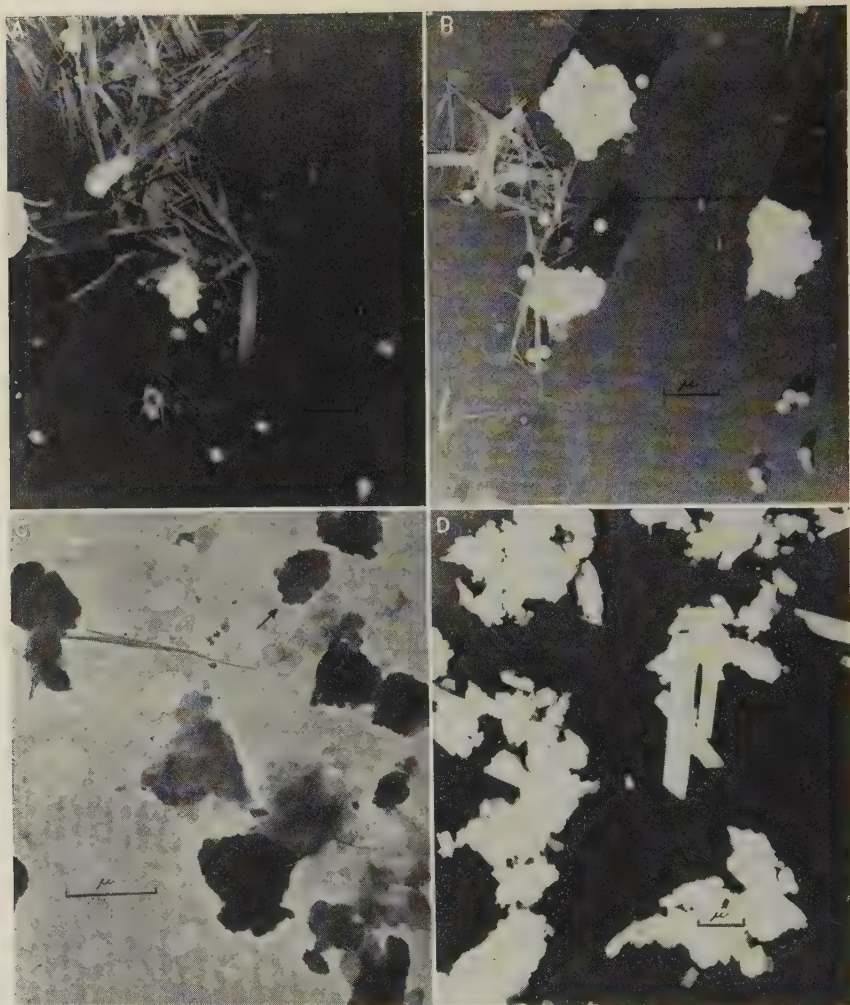


FIG. 6. (A) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. This micrograph, though not representative of the material, is included to show presence of matted fibrous material similar in crystal habit to that of attapulgite. The small cubes may be pyrite, and the platy euhedral aggregate is suggestive of kaolinite. The large opaque shapeless mass is typical of the bulk of the sample. The distorted polystyrene latex particles with attendant shadows are used for internal calibration of particle size. The spheres are approximately 0.25 micron in diameter. (B) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. More of the same material shown in A. Polystyrene latex particles provide an internal calibration for particle-size determination. (C) Ultrafine fraction of lignite separate, Medicine Pole Hills area, Bowman County, N. Dak. An unshadowed mount showing carbonaceous particles up to 1.2 microns in size and admixed clay mineral with shape similar to that of montmorillonite. The platy euhedral aggregate indicated by arrow is suggestive of kaolinite. A few fibrous particles are probably similar to those shown in A and B. (D) Tyuyamunite, San Rafael Swell, Utah. Aggregates of tyuyamunite crystals showing a more elongate habit than that of carnotite in Figure 4B. Distinct prismatic terminations are evident in some of the crystals. Shadowing indicates a lathlike habit. Size of largest laths in the elongate directions is 3 microns.



FIG. 7. (A) Staffelite, Staffel, Germany. This is a replica of a polished surface of stafel-
 felite prepared by the collodion technique. The reader is urged to allow incident light to
 fall on the micrograph from such a direction that the scratch marks appear as depressions.
 This micrograph is characteristic of the surface before treatment with triammonium
 citrate, a preferential etchant for calcium carbonate. (B) This is a similar polished surface
 of staffelite after an hour's immersion in triammonium citrate. Etching is noticeable over
 the entire surface and is more evident along scratch marks. The large pit in the center of
 the micrograph may represent solution of calcium carbonate, or a void in the original surface.
 Preliminary investigation seems to warrant application of the replica technique as a
 means of affording additional data on problems such as the carbonate-apatite problem.
 Sound interpretation of this micrograph can come, however, only after more detailed
 study of surfaces at different orientations, recognition and elimination of possible arti-
 facts, study of other minerals of the apatite group and synthetic products, and employment
 of other replica methods permitting greater resolution. (C) Jarosite from weathered lignite
 collected from the Mendonhall strip mine near Slim Buttes, Harding County, S. Dak. The
 jarosite is pulverulent. No cuboidal crystals could be observed with the optical microscope
 but this micrograph shows readily the typical crystallinity exhibited by this sample of
 jarosite. (D) Jarosite. Enlarged from C.

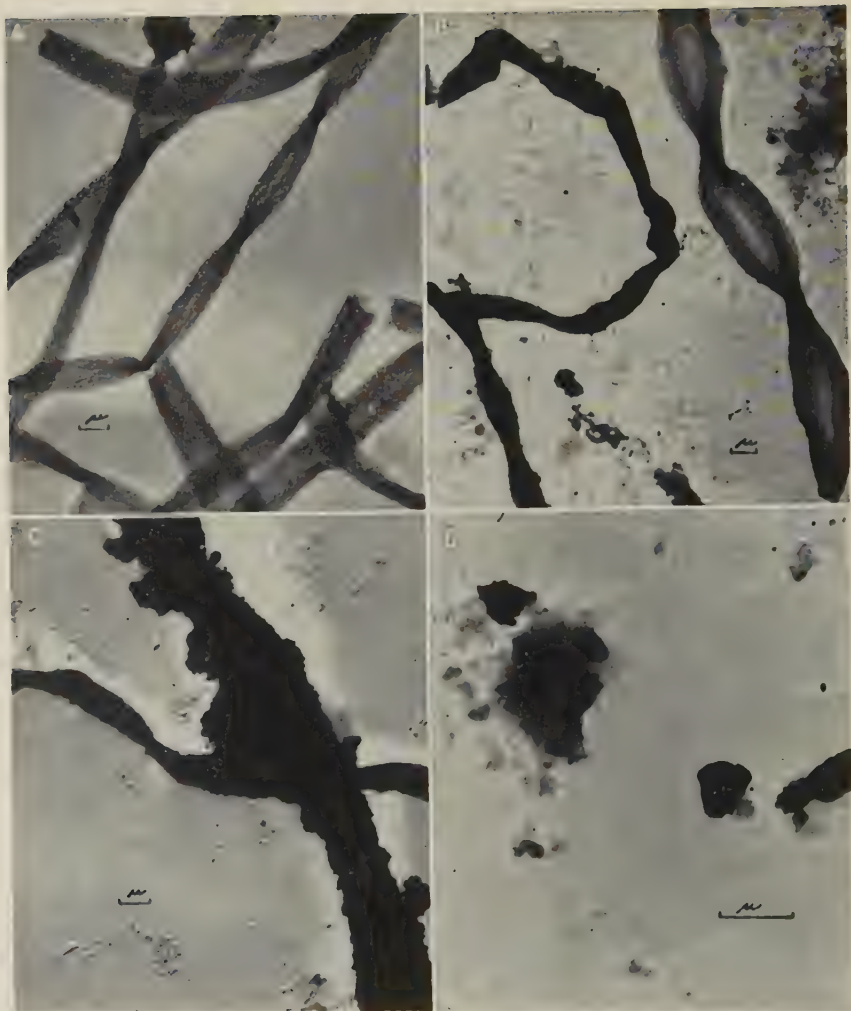


FIG. 8. (A) *Gallionella ferruginea* Ehrenberg, collected from a bog iron deposit from the Montezuma area, Summit County, Colo., by Maurice Deul. Newly formed filament of hydrous ferric oxide showing fibrous nature of the twisted filaments. This is an unshadowed picture but the density of the image is due to the composition of the filaments. (B) *Gallionella ferruginea* Ehrenberg, gradual fossilization of filament on right and more complete fossilization on left. This sample was collected from sludge from the bottom of a stream. (C) *Gallionella ferruginea* Ehrenberg, a fossil filament showing thicker crusts of limonite. (D) Descloizite and montmorillonite, Montrose County, Colo. This micrograph illustrates the application of the microscope in confirming the results obtained by x-ray diffraction and chemical analyses. Chemical analysis of an apparently homogeneous sample of montmorillonite showed an unusually high lead content. An x-ray powder mount yielded a good montmorillonite pattern. Close inspection of the pattern revealed a few faint lines with spacings similar to descloizite. Examination in the electron microscope showed thin transparent laths and aggregates suggestive of a montmorillonite group species and subhedral dense particles presumed to be descloizite. The latter particles were fused readily on exposure to the more intense electron beam, a property characteristic of descloizite.

BADDELEYITE FROM PHALABORWA, EASTERN TRANSVAAL¹

S. A. HIEMSTRA, *Geological Survey, Pretoria, South Africa.*

ABSTRACT

The rare mineral baddeleyite occurs at Phalaborwa² in the Eastern Transvaal. It has a density of $D_{25} = 5.739 \pm 0.005$. The optical properties are:

$$\alpha = 2.136 \pm 0.005$$

$$\beta = 2.236 \pm 0.008$$

$$\gamma = 2.243 \pm 0.008$$

$$2V_{\alpha} = 30^{\circ} \pm \frac{1}{2}^{\circ}$$

$$X \wedge c = 13^{\circ}$$

An x-ray diffraction pattern and a chemical analysis are given.

INTRODUCTION

Baddeleyite (natural zirconia) was identified among the heavy minerals in a radioactive talus sample submitted to the author for examination by Dr. D. J. Simpson of the Geological Unit, Atomic Energy Board, in August, 1952. The associated minerals were large lumps of magnetite, notable amounts of apatite and small quantities of diopside and phlogopite. Zircon, uranoan thorianite and baddeleyite were minor constituents.

In the field the radioactivity was traced to carbonatite rocks³ by the geological unit of the Atomic Energy Board. The carbonatites are composed of large irregular fragments of magnetite, calcite, yellowish chondrodite and apatite, with smaller amounts of phlogopite, chalcocite,⁴ chalcopyrite and thorianite. Baddeleyite is a minor constituent.

PREVIOUS WORK

L. Fletcher⁵ published a description of a single broken crystal of baddeleyite from Ceylon. A crystallographic description in which he established the monoclinic symmetry is followed by a few optical observations on thin splinters of the mineral. Interference figures showed him the presence of inclined dispersion. His data are as follows on page 276.

¹ Published with the consent of the Department of Mines, and the Atomic Energy Board.

² This is the spelling of Palabora, recently adopted in the Union of South Africa.

³ That these calcite-rich rocks are carbonatites was largely established from field relationships by Mr. H. D. Russell who undertook detailed mapping of the area.

⁴ The chalcocite and chalcopyrite in this rock were identified by Mr. D. Groeneveld of this office. (Unpublished report)

⁵ Fletcher, L., *Mineral. Mag.*, **10**, 148 (1893).

$$X \wedge c = 13^\circ$$

$$\text{Apparent axial angle} = 70^\circ - 75^\circ$$

X is yellow; Y is green.

$$\text{Absorption } X > Y > Z$$

$$D = 6.025$$

Blake and Smith⁶ published their crystallographical measurements of two crystals in 1907. They found specific gravities of 5.72, 5.73 and 5.82 on three different crystals.

The last crystal (specific gravity 5.82) was used by Kathleen Yardley⁷ in her determination of the dimensions of the unit cell, viz: $a = 5.21$; $b = 5.26$; $c = 5.375$; $\beta = 80^\circ 32'$. She found that, by assuming a molecular weight of 128 for this crystal (pure zirconia 123.22), a better agreement between calculated and determined spacings was obtained. The heavier impurity could be hafnia.

Using the intensities of the x-ray reflections reported by Yardley, Náray-Szabó⁸ was able to deduce the coordinates of the ions in baddeleyite.

Larsen and Berman⁹ reported refractive indices of 2.13, 2.20 and 2.19 for α , γ and β respectively, an axial angle of 30° , and rather strong dispersion with $r > v$.

The various publications of Hussak, and Hussak and Reitingner were not available to the author.

HABIT

The baddeleyite from Phalaborwa occurs typically in the form of short black prismatic crystals, mostly between 0.05 and 1 mm. in their longest dimensions. The crystals are usually flattened parallel to $\{100\}$, and in addition show faces of $\{110\}$ and $\{011\}$. Untwinned crystals are rare. Vertical striae caused by polysynthetic twinning with $\{001\}$ as the composition plane can usually be seen on faces in the $[001]$ zone, particularly on the prism faces (Fig. 1).

In thin sections cleavages were observed parallel to $\{001\}$ and $\{010\}$.

DENSITY

Pycnometers of suitable size were not available. An acceptable accuracy could be obtained by the following method however.

The bottom of a small test tube, fitted with a notch from which it could be suspended vertically on a chemical balance, was used. It was weighed

⁶ Blake, G. S., and Smith, H. G. F., *Mineral. Mag.*, **14**, 378 (1907).

⁷ Yardley, K., *Mineral. Mag.*, **21**, 169 (1928).

⁸ Náray-Szabó, St. v., *Zeit. Krist.*, **94**, 414 (1936).

⁹ Larsen, E. S., and Berman, H., *U. S. Dept. of the Interior, Bull.* **848**, 210 (1934).

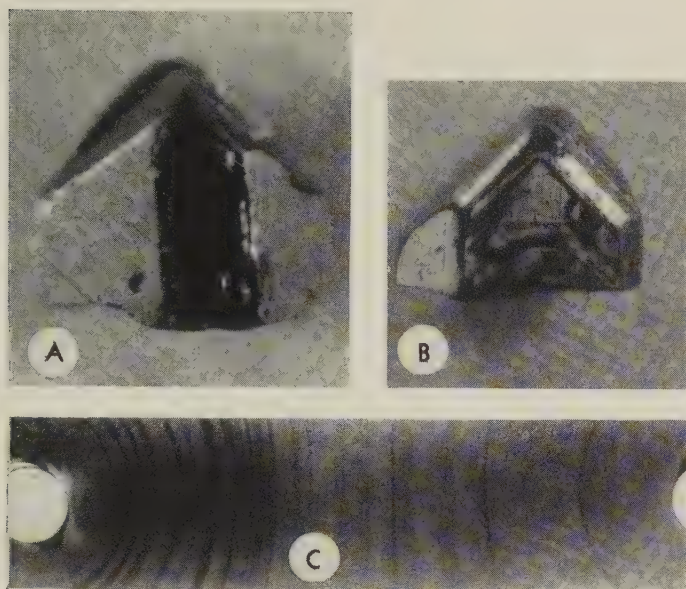


FIG. 1. *A.* Untwinned crystal of baddeleyite. ($\times 40$) *B.* Twinned crystal of baddeleyite, showing vertical striae on the prism and orthopinocoid faces. ($\times 40$). *C.* X-ray diffraction pattern of baddeleyite. Unfiltered Cu-radiation. 1 mm. = $1^\circ \theta$.

when dry, and also when suspended by means of a hair in boiled distilled water of known temperature. A small quantity of pure cleaned baddeleyite crystals (usually between 2 and 5 gm.) was introduced into the dried tube, and the tube with crystals weighed again when dry, and when suspended in boiled distilled water. Weighing after drying showed that no material was lost during the above process.

It was found to be essential however to remove all air bubbles before weighing in water. This could be done by boiling while the pressure was diminished by means of an air suction pump.

Corrections were applied for the air displaced by the weights, and for the density of the distilled water at the temperatures where observations were made.

Three determinations on different portions of material at different times gave values of 5.740, 5.737 and 5.739. The finally adopted value is:

$$D_{25}^{25} = 5.739 \pm 0.005.$$

OPTICAL PROPERTIES

Yellow phosphorus was used as an immersion medium for the determination of the refractive indices. After melting under water mounts

could be made with clear phosphorus which usually remained fluid in an undercooled condition for a minute or two in which the necessary observations had to be made. As determined in a prism on a one-circle goniometer, the refractive index of liquid phosphorus varies from 2.07 for red light to 2.17 for violet light (2.085 for sodium light at 25° C., the room temperature). During crystallization to an isotropic mass, the index increased to 2.12 for red light, and 2.22 for violet light (2.139 for sodium light at room temperature).

Using a monochromator, α could be matched with the index of undercooled phosphorus by changing the wave-length. It is considered that the error in the value of 2.136 so obtained is of the order of 0.005.

When using solid phosphorus, a clear Becke line could not be obtained and no accurate determinations were possible. It could be established however that β and γ are both higher than the highest values attainable in solid phosphorus, namely 2.22.

Knowing α fairly accurately, it only remained to determine two of the main double refractions so as to calculate β and γ .

Utilizing small crystals, orientated sections were cut in such a way that Z and X, or Z and Y were in the section plane. Using a Berek compensator, the relative retardation was determined in sodium light.

It was found difficult to prepare sections perpendicular to Y thin enough to enable one to turn the compensator drum to the position of compensation. Readings were therefore made on any "nth" compensation band. The retardation so determined differs from the wanted retardation by the amount $n\lambda$, (where λ =the wave-length of the light used).¹⁰ It can therefore easily be calculated.

Thickness determinations by focussing on the top of the glass mount and on the top of the sections were inaccurate. The section and its glass mount were therefore ground away perpendicular to the section plane, until the exact spot where the retardation was determined came into view. They were now mounted on a microscope with the newly ground surface parallel to the microscope stage. Using a graduated ocular and high power objective, the thickness could be measured directly. The retardation divided by the thickness gave the amount of the double refractions ($\gamma-\alpha$) and ($\gamma-\beta$) equal to 0.100 and 0.007, respectively. The error in these values is thought to be less than 0.003.

The axial angle was measured on the universal stage which was fitted with glass hemispheres of high refractive index to decrease the difference between measured and true angles. The corrected value of 30° so ob-

¹⁰ Burri, C., *Das Polarisationsmikroskop*, E. Birkhäuser & Cie., AG., Basel, (1950), p. 143.

tained could be duplicated to within $\frac{1}{2}^\circ$ by repeated measurements. The value of 28° calculated from the refractive indices is in better agreement than could be expected from the errors assumed in the determination of α , β and γ .

Measuring the axial angle in light having wave-lengths equal to the Fraunhofer lines *F*, *D* and *C*, revealed that the amount of dispersion is less than the experimental error. A slightly smaller mean value ($29\frac{3}{4}^\circ$) was obtained in blue light however. This indicates that $r > v$, to the extent of roughly $\frac{1}{2}^\circ$.

The angle between *X* and *c* was measured in a section of a twinned crystal cut parallel to {010}. The angle between the position of extinction and the composition planes increased from 12.6° to 13.0° for the Fraunhofer lines *F* and *C*, respectively.

To summarize, the optical properties are as follows:

<i>Refractive indices</i>	<i>Pleochroism</i>
$\alpha = 2.136 \pm 0.005$	<i>X</i> = dark brown
$\beta = 2.236 \pm 0.008$	<i>Y</i> = brown
$\gamma = 2.243 \pm 0.008$	<i>Z</i> = light brown
<i>Orientation</i>	<i>Axial angle</i>
$X \wedge c = 12.6^\circ (F)$	$2V_\alpha = 30^\circ \pm \frac{1}{2}^\circ$ (measured)
$X \wedge c = 12.8^\circ (D)$	
$X \wedge c = 13.0^\circ (C)$	$2V_\alpha = 28^\circ$ (calculated)
<i>Y</i> = <i>b</i>	$r > v$

The values for β and γ are considerably higher than those determined by Larsen⁹. His values, however, are not in good agreement with his axial angle of 30° .

CHEMICAL ANALYSIS

About 5 gm. of carefully handpicked material was submitted for quantitative chemical analysis. No other minerals were detected under the microscope, but small inclusions were possibly present. The elements found in addition to zirconium (Table 1) are all major constituents of the minerals associated with the baddeleyite, excepting titanium and manganese. Small amounts of Fe^3 have been reported as substituting for Zr^4 in baddeleyite.¹¹ Comparing the ionic radii of Fe^3 (0.64) and Ti^4 (0.68) with that of Zr^4 (0.79),¹² it can be seen that the differences are appreciable. Ti^4 will probably enter the crystal lattice more readily than Fe^3 , be-

¹¹ Hevesy and Jantzen, *Zeit. anorg. Chem.*, **136**, 387 (1924), as mentioned by Palache, C., Berman, H., and Frondel, C., in Dana's System of Mineralogy, 7th. edition, Vol. 1, p. 609.

¹² The values for the ionic radii were taken from Green, *J. Bull. Geol. Soc. Am.*, **64**, 1001-1012 (1953).

TABLE 1. CHEMICAL ANALYSIS OF BADDELEYITE FROM PHALABORWA
(Abraham Kruger, *Analyst*)

	Per Cent
ZrO ₂	95.20
SiO ₂	0.06
Fe ₂ O ₃	2.10
MgO	0.64
CaO	0.80
MnO	0.23
TiO ₂	1.65
Ignition lost	0.00
Total	100.68

cause of its slightly larger radius, and also because its valence is the same as that of Zr⁴. The radius of Mn² (0.80) is close to that of Zr⁴.

Using the cell dimensions reported by Yardley,⁷ the density determined by the writer, and a value of 6.0597×10^{23} for Avogrado's number,¹³ the molecular weight of the baddeleyite was calculated and found to be 126. (Pure zirconia, 123.22.) If this calculated value is correct, then an appreciable amount of what was represented as ZrO₂ in the analysis actually consists of HfO₂. (Mol. weight 210.6.) Assuming that the determined amounts of the lighter molecules Fe₂O₃, MgO, MnO and TiO₂ are present within the baddeleyite molecule, then the highest amount of HfO₂ that can be present, is 10%. If smaller amounts of the lighter molecules are present in the crystal lattice, then a correspondingly smaller amount of hafnia is necessary for a molecular weight of 126.

X-RAY DIFFRACTION PATTERNS

X-ray powder diffraction photographs were taken in cameras having diameters of 114.7 mm. and 57.3 mm. The films were mounted according to the method of Ievens and Straumanis. Unfiltered copper radiation produced at 35 K.V. and 20 ma. was used. A large number of lines, most of them of low intensity, and somewhat diffuse, was obtained (Fig. 1). Corrections were applied for the shrinkage of the film.

In Table 2 the *d*-values obtained by the author are compared with those reported by Yardley. No other set of values is known to the author.

ACKNOWLEDGMENTS

The writer is grateful to Dr. B. Wasserstein who reviewed the manuscript, and to Dr. D. J. Simpson for the material from which the mineral was obtained.

¹³ Schlecht, W. G., *Am. Mineral.*, **29**, 108 (1944).

TABLE 2. COMPARISON OF DIFFRACTION PATTERNS OF BADDELEYITE

Hiemstra		Yardley		
<i>Intensity</i> (Estimated)	<i>d.</i> (Å)	<i>Intensity</i>	<i>d.</i> ¹⁴ (Å)	<i>hkl</i>
2	5.08			
2	4.05			
4	3.66	W	3.674	011
4	3.51			
10	3.15	V.S.	3.164	11 $\bar{1}$
9	2.835	S.	2.831	111
5	2.62	M.S.	2.616	020 002
2	2.54	M.W.	2.540	200
$\frac{1}{2}$	2.44			
1	2.33	W.	2.333	012 021
3	2.21	M.	2.205	21 $\bar{1}$ 102
2	2.18			
3	2.02	M.W.	2.006	112 202 211
2	1.990			
4	1.847	M.S.	1.849	022
5	1.817	M.S.	1.810	21 $\bar{2}$ 220 12 $\bar{2}$
1	1.779			
2	1.688	M.	1.693	30 $\bar{1}$ 300 202
3	1.652	M.	1.658	221 013 11 $\bar{3}$
1	1.639			
1	1.609	V.W.	1.610	31 $\bar{1}$ 310
1	1.589			
3	1.541	M.W.	1.540	30 $\bar{2}$ 131
1	1.506	W.	1.510	113
1	1.498			
2	1.476	W.	1.474	311
$\frac{1}{2}$	1.447	V.W.	1.450	023
2	1.420			
$\frac{1}{2}$	1.360			
2	1.324			
2	1.263			
$\frac{1}{2}$	1.247			
$\frac{1}{2}$	1.228			
1	1.212			
1	1.177			
1	1.166			
1	1.160			
1	1.151			
1	1.140			
1	1.139			

Hiemstra		Yardley		
<i>Intensity</i> (Estimated)	<i>d.</i> (Å)	<i>Intensity</i>	<i>d.</i> ¹⁴ (Å)	<i>hkl</i>
1	1.115			
1	1.105			
1	1.091			
1	1.054			
1	1.044			
2	1.036			
1	1.011			
1	0.9995			
1	0.9952			
1	0.9810			
1	0.9618			
1	0.9458			
1	0.9369			
1	0.9291			
$\frac{1}{4}$	0.9226			
$\frac{1}{2}$	0.9046			
$\frac{1}{2}$	0.8981			
3	0.8859			
$\frac{1}{2}$	0.8777			
$\frac{1}{4}$	0.8688			
$\frac{1}{4}$	0.8626			
$\frac{1}{2}$	0.8552			
1	0.8465			
$\frac{1}{2}$	0.8360			
$\frac{1}{2}$	0.8293			
$\frac{1}{2}$	0.8236			
$\frac{1}{4}$	0.8184			
$\frac{1}{5}$	0.8129			
4	0.8059			
1	0.8037			
$\frac{1}{2}$	0.8007			
$\frac{1}{2}$	0.7994			
$\frac{1}{2}$	0.7937			
$\frac{1}{3}$	0.7918			
$\frac{1}{2}$	0.7776			
$\frac{1}{4}$	0.7755			

¹⁴ These values were converted from Siegbahn units to Ångströms by the writer.

MEMORIAL OF LAWSON H. BAUER

CLIFFORD FRONDEL, *Harvard University, Cambridge, Mass.*

Lawson H. Bauer, for over 40 years chemist and finally Chief Chemist to the New Jersey Zinc Company at Franklin, New Jersey, died at the Franklin Hospital on January 27, 1954. Mr. Bauer was born at Mertztown, Pennsylvania, on August 18, 1889. After graduation from High School in Kutztown in 1905 he taught school for two years in Lehigh County, Pennsylvania, and then entered Lafayette College. An honor



LAWSON H. BAUER
1889-1954

student and member of Phi Beta Kappa, he graduated in 1911. Following several years of work in industrial laboratories in Maryland he entered the employment of the New Jersey Zinc Company at Franklin in 1913. Here, aside from his official duties, he was active in civic affairs in the town, as a member of the Board of Education and as President for many years of the Board of Health. Mr. Bauer's wife died in 1953. He is survived by two sons and two daughters.

The death of Mr. Bauer followed by the final closing in October, 1954,

of the Franklin mine after more than a century of operation and the death late in 1954 of Professor Charles Palache mark the end of an era in Franklin mineralogy. Mr. Bauer contributed directly through his analytical work to the mineralogy of the famous deposit that he knew so well, but his most important contribution, stemming from the unselfish and truly scientific desire to bring the mineralogy of Franklin to description and interpretation, was in aiding the flow of specimen material from the Franklin and Sterling Hill mines to investigators and collectors over the world. Very little is publically known of the details of these great and unique deposits, and the knowledge that has been gained has come in considerable part from his efforts in this regard, made with the permission of the Zinc Company, and the activities of earlier collectors such as Hancock and Roebing.

Mr. Bauer published 18 mineralogical papers, all written in cooperation with other people. These included the description of 8 new mineral species: cahnite, larsenite, calcium larsenite, mcgovernite, loseyite, mooreite, yeatmanite and manganpyrosmalite. Many of these and other new species were first recognized by Bauer, chiefly from specimens obtained on the picking table—that almost unreachable Mecca of collectors—or from miners. The monographic work by Charles Palache, “The Minerals of Franklin and Sterling Hill, Sussex County, New Jersey,” published in 1935 as Professional Paper 180 of the U. S. Geological Survey, contains over 70 analyses by Bauer, in part made jointly with his associate David Jenkins. A number of additional analyses have appeared in more recent publications. There are also many as yet unpublished analyses, all carefully preserved on labels glued to specimens in his personal collection. This collection, although small as compared to others amassed at Franklin, contained many type specimens and others of outstanding beauty or rarity. Among the latter are the finest known specimen of hodgkinsonite and the extraordinary twinned crystal of cahnite figured in Palache’s work. The collection was purchased from Mr. Bauer’s estate jointly by the U. S. National Museum and Harvard University.

Those collectors or students who visited Mr. Bauer’s home to see his collection usually were grilled over the identity of a suite of about 60 specimens kept in a special tray. All were of identical size, although of very unlike color and appearance, and all observers were dismayed to be finally informed that only one species was represented, willemite. The less common Franklin minerals are much more troublesome, and innumerable identifications have been accepted solely on the authority that “Bauer said so.”

Mr. Bauer became a member of the Mineralogical Society of America

in 1929 and he was elected a Fellow in 1932. His work is part of the history of Franklin, and warm personal memories will be carried by those fortunate to have known this spirited man.

BIBLIOGRAPHY

- BAUER, L. H. (with J. V. LEWIS), Cyprine and associated minerals from the zinc mine at Franklin, N. J.: *Am. J. Sci.*, **4**, 249 (1922).
- (with C. PALACHE), Hyalophane from Franklin Furnace, N. J.: *Am. Mineral.*, **11**, 172 (1926).
- (with H. BERMAN), Löllingite from Franklin, N. J.: *Am. Mineral.*, **12**, 39 (1927).
- (with C. PALACHE), Cahnite, a new boroarsenate of calcium from Franklin, N. J.: *Am. Mineral.*, **12**, 149 (1927).
- (with C. PALACHE), Mcgovernite, a new mineral from Sterling Hill, N. J.: *Am. Mineral.*, **12**, 373 (1927).
- (with C. PALACHE AND H. BERMAN), Larsenite and calcium larsenite, a new member of the chrysolite group from Franklin, N. J.: *Am. Mineral.*, **13**, 142 (1928).
- (with C. PALACHE AND H. BERMAN), Larsenite, calcium larsenite and the associated minerals at Franklin, N. J.: *Am. Mineral.*, **13**, 334 (1928).
- (with H. BERMAN), Friedelite, schallerite, and related minerals: *Am. Mineral.*, **13**, 341 (1928).
- (with E. S. LARSEN AND H. BERMAN), Norbergite from Franklin, N. J.: *Am. Mineral.*, **13**, 349 (1928).
- (with H. BERMAN), Loseyite, a new Franklin mineral: *Am. Mineral.*, **14**, 150 (1929).
- (with H. BERMAN), Mooreite, a new mineral, and fluoborite from Sterling Hill, N. J.: *Am. Mineral.*, **14**, 165 (1929).
- (with C. PALACHE), On the occurrence of beryllium in the zinc deposits of Franklin, N. J.: *Am. Mineral.*, **15**, 30 (1929).
- (with H. BERMAN), Notes on some Franklin minerals: *Am. Mineral.*, **15**, 340 (1930).
- (with H. BERMAN), Barium-muscovite from Franklin, N. J.: *Am. Mineral.*, **18**, 30 (1933).
- (with C. PALACHE AND H. BERMAN), Yeatmanite and sarkinite from Franklin, N. J.: *Am. Mineral.*, **23**, 527 (1938).
- (with C. FRONDEL), Nasonite and its relation to pyromorphite: *Am. Mineral.*, **36**, 534 (1951).
- (with C. FRONDEL), Manganpyrosomalite and its polymorphic relation to friedelite and schallerite: *Am. Mineral.*, **38**, 755 (1953).
- (with C. FRONDEL), Kutnahorite, a manganese dolomite, $\text{CaMn}(\text{CO}_3)_2$: *Am. Mineral.*, in press (1955).

MEMORIAL OF MAGNUS VONSEN¹

GEORGE SWITZER, *U. S. National Museum, Washington, D. C.*

The death of Magnus Vonsen on June 16, 1954, left a gap in the ranks of American mineralogists that will not soon be filled. Mineralogy was his avocation, not his profession. Even so, an unusually keen interest in his hobby over a period of forty years resulted in many important contributions to the science and won for him a position of highest esteem amongst both scientists and mineral collectors.

Vonsen was born in Petaluma, California, in 1879. His father, John Vonsen was a rancher, and Vonsen spent his early years on the home ranch near Petaluma. His career in the feed and grain business began in 1904 when he became part owner of a store in Petaluma. In 1913 he became sole owner and organized the M. Vonsen Company. Vonsen was a very able business man and under his direction the business prospered and grew to have several branch stores in nearby towns.

In 1906 Mr. Vonsen was married to Bertha E. Petersen of Petaluma. She and a daughter survive him.

Vonsen became interested in minerals during World War I when the demand for chrome, manganese and mercury stimulated mining activity in the vicinity of Petaluma. His mineral collection, begun at this time, grew to be one of major importance. At the time of his death it was generally considered to be the finest private mineral collection in the United States.

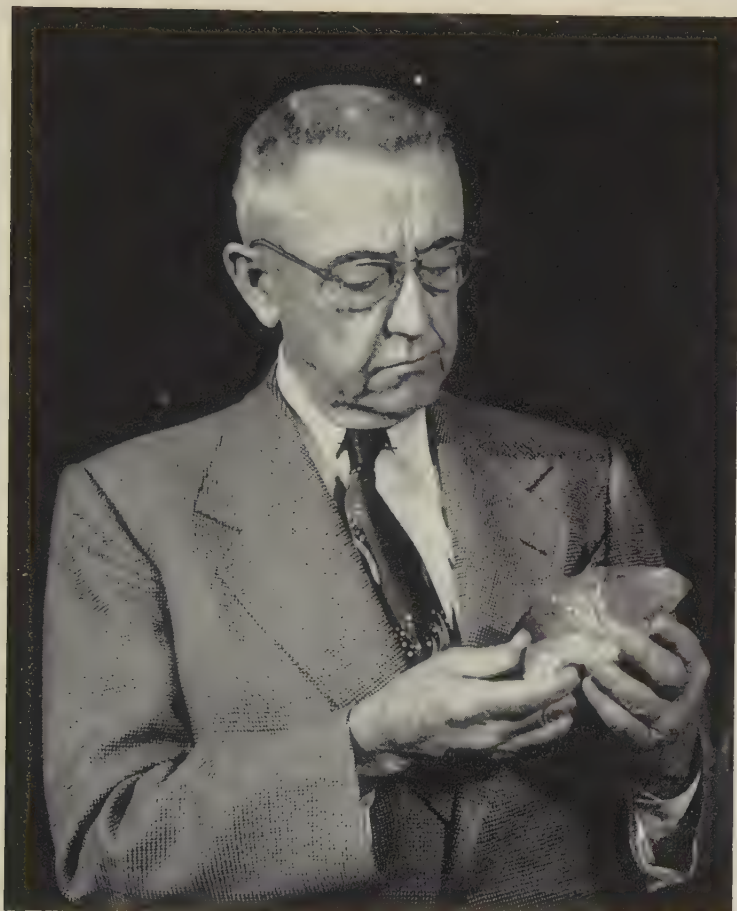
His collection was housed in museum-type cases in a special room in his home. It was a revelation to all who saw it, for every specimen was of superb quality and beautifully displayed.

The collection is especially noteworthy for its borate minerals, for Vonsen was particularly interested in this mineral group. He made twice-yearly collecting trips to Death Valley and nearby areas for more than thirty years. His knowledge of mineral localities in southeastern California and southwestern Nevada was unsurpassed. Specimens of borate minerals in his collection are the finest in the world.

Vonsen received no formal schooling in science. His mineralogy was learned by study at home and through a University of California extension course. He had a fully equipped home laboratory and developed great skill in qualitative chemical analysis and in the use of the polarizing microscope.

One of Vonsen's first contributions to the science of mineralogy was the discovery near Riverside, California, of a new iron magnesium borate.

¹ Publication authorized by the Secretary, Smithsonian Institution, Washington, D. C.



(Photograph by Tashio Asaeda)

MAGNUS VONSEN

1879-1954

It was named vonsenite in his honor by A. S. Eakle in 1920. He discovered a second new borate mineral at Borax Lake, Lake County, California, in 1934. It was named teepleite, and described in a paper which he co-authored with W. A. Gale and W. F. Foshag.

The California glaucophane schists attracted a great deal of Vonsen's attention. He was the first to discover pumpellyite as a constituent of these rocks. He also first demonstrated that in them lawsonite is widely distributed and occurs in a number of dissimilar forms and associations.

The saline minerals were also of particular interest to him. His col-

lections from Searles Lake, Borax Lake and many other similar areas in California and Nevada, are the most complete anywhere.

Mr. Vonsen was a close friend of Drs. Palache, Larsen, Schaller and Foshag. He derived great pleasure from visits to his home by these and other mineralogists, who came to see his collection and to accompany him on field trips. His finds on collecting trips were always shared with others. The collections at Harvard and the U. S. National Museum contain many outstanding specimens contributed by him.

In 1931 Vonsen became a member of the California Academy of Sciences, and a few years later was made Honorary Curator of Minerals of the Academy. In December of 1953 he donated part of his collection to the Academy and saw it installed in handsome new cases in the Hall of Science, in Golden Gate Park, San Francisco. In his will he provided that the balance of the collection shall go to the Academy, thus giving California its first outstanding public mineral collection.

Vonsen was a businessman, and his remarkable accomplishments in his hobby were made only in hard-won leisure time. Even so, he also found opportunity to take an active part in civic affairs, in particular the Red Cross and the Boy Scouts of America. He was also intensely interested in plans to erect an earth-fill barrier across a northern arm of San Francisco Bay, and he devoted much time and energy to this project.

I cannot conclude this sketch of the life of Magnus Vonsen without expressing my own great sense of loss in his passing. I grew up just a few houses down the street from Mr. Vonsen. He kindled my interest in mineralogy when I was twelve years of age, and during my junior and senior high school years, I spent countless fascinating evenings in his laboratory watching him work and listening to him talk about minerals and tell of his collecting experiences. Other times were spent studying his collections or accompanying him on collecting trips. In later years his help, advice, and constant encouragement proved invaluable to me. I am but one of many who mourn the loss of a dear and faithful friend.

PUBLISHED PAPERS OF MAGNUS VONSEN

- Death Valley and the borates of California, *Rocks and Minerals*, **3**, 73-77 (1929).
Pumpellyite from California, *Am. Mineral.*, **17**, 338-342 (1932): (with Irving, John, and Gonyer, F. A.).
The discovery of borates in California, *The Mineralogist*, **3**, 3-4 (1935).
Borax Lake, California, *Calif. Div. Mines Rept.*, **32**, 98-108 (1936): (and Hanna, G. D.).
Teepleite, a new mineral from Borax Lake, California, *Am. Mineral.*, **24**, 48-52 (1939): (with Gale, W. A., and Foshag, W. F.).
Preliminary report on minerals of geysers of Sonoma County, California, *The Mineralogist*, **9**, 245-248 (1941).
Minerals at "The Geysers," Sonoma County, California, *Calif. Jour. Mines and Geol., Report 42 of the State Mineral.*, 287-293 (1946).
Borates of California, *Rocks and Minerals*, **26**, 494-503 (1951).

PRESENTATION OF THE ROEBLING MEDAL OF
THE MINERALOGICAL SOCIETY OF AMERICA
TO CECIL EDGAR TILLEY

ARTHUR F. BUDDINGTON, *Princeton University, Princeton,
New Jersey.*

*Mr. President, Fellows and Members of the Mineralogical Society of
America and Guests:*

The Roebling medal is for meritorious achievement in the fields of the Mineralogical Sciences. Recalling the interest of Colonel Roebling in acquiring specimens of all new minerals for addition to his comprehensive collections, I am sure that were he now alive our medalist of today would be *well* and *most favorably* known to him. For not only does the medalist have a mineral, *tilleyite*, named in his honor but he is himself the discoverer and describer of 7 new minerals.

Professor Tilley is the third medalist to be chosen from Great Britain, the other two being L. J. Spencer and Sir Lawrence Bragg. Also, peculiarly enough, like Sir Lawrence Bragg, he was born in Adelaide, South Australia. His undergraduate education was received at the Universities of Adelaide and Sydney. He served as Demonstrator in Geology and Mineralogy at the University of Sydney in 1916 and as chemist to the Department of Explosives Supply, Queensferry, 1917-1918. Later he attended Cambridge University, England, and received the Ph.D. in 1923. From 1928 to 1931 he was Lecturer in Petrology at the University of Cambridge. Alfred Harker who was Reader in Petrology in the Geology Department of the Sedgewick Museum, retired in 1931. At this time Petrology was combined with the Department of Mineralogy and Tilley became the first Professor of the Department of Mineralogy and Petrology at Cambridge, a post he still holds.

Professor Tilley's publications, around 60 in all, from the very first to the very last are characterized by a percipient application of the data and principles of physical chemistry and of integrated geologic knowledge to the interpretation of the phenomena of mineral associations and of rocks. He is the first recipient of the Roebling medal who has made a study of the minerals and mineral assemblages of metamorphism a major part of his researches.

One of his earliest publications (1920) dealt with metamorphism, reconstitution and decarbonation of Precambrian dolomites of the Southern Eyre Peninsula, South Australia. Two of his major series of researches subsequently have dealt with related phenomena, the contact metamorphic zones between dolerite and limestone at Scawt Hill, An-

trim, Ireland, and at Camas Mor, Muck, and between granite and limestone near Broadford in Skye, Scotland. The extent to which Tilley has been able to develop new data and principles of general significance from intensely detailed studies of rocks, some of which many of us would have passed up as hardly worth a second look, is amazing. Besides his discovery of 5 new minerals of Scawt Hill and one new mineral at Broadford he extended the stages represented in thermal metamorphism by three, showing that talc belongs at the earliest stage, that tilleyite belongs between åkermanite and spurrite, and rankinite between spurrite and merwinite as the temperature is raised. He also demonstrated that on a small scale basic feldspathoidal rocks were formed by reaction of basaltic igneous magma with carbonate sediments and that mildly alkali assemblages and even some desilication were produced by reaction of granite magma with limestone.

The name of the island, Muck, which was the site of one of Tilley's studies, reminds me of a joke which he told. There are three islands grouped together and known locally as the Hebridean cocktail: Eigg, Muck, and Rum. I do not wish, however, to imply in any degree whatever that Tilley's imaginative and creative ideas were stimulated by such a concoction. I have seen him maintain his normal warm good nature and make his usual sly humorous pithy comments in wind, rain and chill without benefit of the cup that cheers.

Professor Tilley has been one of the pioneers in and major contributors to the development of our ideas, understanding and classification of metamorphic rocks in the light of the "Facies concept" as now developed. The fundamental physico-chemical basis was suggested by Goldschmidt in 1911. The idea was amplified and applied in general by Eskola in 1920. Beginning in 1923 we have a long series of papers by Tilley dealing with specific examples of the variation of mineral assemblages where on the one hand the range of physical conditions is similar, or to use his term, is isograde, and the bulk chemical composition varies; and on the other hand where the bulk chemical composition remains similar and the range of physical conditions varies. For the latter he was able to suggest particular chemical reactions by which one mineral assemblage was transformed to another as the temperature changed. He also integrated geology with laboratory studies in his researches on progressive regional metamorphism. The mapping of metamorphic zones originally begun by Barrow in the southern and eastern Scottish Highlands was greatly extended by Tilley (1925) and by Elles and Tilley (1930). In these classic papers the hypothesis was developed that the isograd surfaces of metamorphism may be discordant with the stratigraphic layers of the folded rocks and that the superposed zones of metamorphism might themselves

be folded so that rocks reconstituted at a higher temperature came to overlie those formed at a lower temperature.

Nearly every petrologist sooner or later engages in a study of the alkalic rocks, a group so insignificant in volume, so enigmatic in origin and so attractive to one's curiosity. Tilley is no exception. He spent a year at the Geophysical Laboratory in Washington undertaking experimental studies in the ternary system, $\text{Na}_2\text{SiO}_3\text{-Na}_2\text{Si}_2\text{O}_5\text{-NaAlSiO}_4$ and published the results in 1933. In recent years he has renewed his interest in the subject and after a review of the variation of the chemical composition of nepheline with variation of composition of the system in which it formed, concluded that the composition of magmatic nepheline solid solutions is primarily conditioned by chemical composition of the environment, but that nepheline of metasomatic origin may involve a different story. He is now completing studies of the nepheline syenites of Eastern Canada based on field studies in 1950.

In 1921 Tilley published a paper on an Australian tholeiitic basalt. Nothing further by him on this subject appeared for years, but it is obvious that it was not forgotten. In 1950, after a period of 29 years of incubation and growth in the depths of his mind, there blossomed forth as a presidential address a fully matured exposition of the role of tholeiitic basalt type of lava as the closest approach to the primary magma of the Hawaiian alkali magma series in particular and the ocean basins in general. The reverberations from this hypothesis are still going on in the petrological world.

Professor Tilley has received many honors for his professional accomplishments and distinguished recognition for his high capacity in human affairs. He was Exhibition Scholar at Cambridge, 1920-1924, recipient of the Sedgwick Prize (1931) and Bigsby Medal (1937), elected to the Royal Society of London (1938), an honorary member of the Royal Geological Society of Cornwall and Foreign Correspondent of the Geological Societies of America, of Sweden and of our own Mineralogical Society of America. He has served as President of the Mineralogical Society of London, (1948-1951), President of the Geological Society of London (1949-1950), Vice-President of the Royal Society of London (1949-1950), and has recently been elected Vice-Master of Emmanuel College, Cambridge.

Mr. President, it is a privilege to present Cecil Edgar Tilley as the recipient of the Washington A. Roebling Medal of The Mineralogical Society of America.

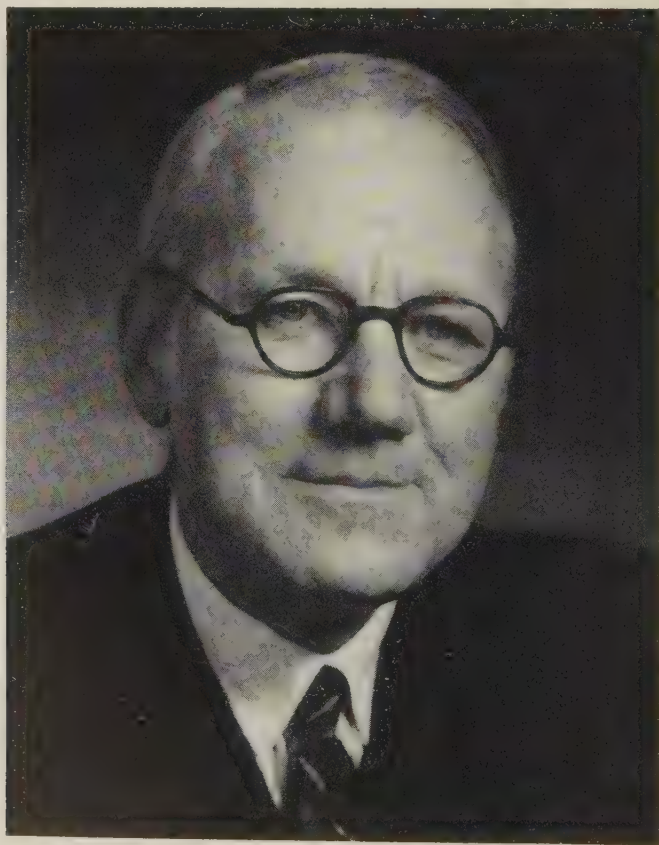
ACCEPTANCE OF THE ROEBLING MEDAL OF THE MINERALOGICAL SOCIETY OF AMERICA

CECIL EDGAR TILLEY, *University of Cambridge, Cambridge, England.*

Mr. President, Professor Buddington, Fellows and Members of the Mineralogical Society, Guests:

The Mineralogical Society has bestowed a very great honour upon me with the award of the Roebling Medal, and it is with the sincerest appreciation that I would wish to record my thanks to the Council for their most generous estimate of my merits.

When I survey the roll of former recipients of this medal I am very conscious of my own shortcomings, and if the fact that I am the thir-



CECIL EDGAR TILLEY

Recipient of the Roebling medal of the Mineralogical Society of America.

teenth recipient engenders in me a double awareness, I may be forgiven if I am grateful that today is not also Friday.

The occasion is one inviting retrospect and I may be permitted a personal note.

Looking back through the years I realize that my lot has fallen in pleasant places. I was particularly fortunate and privileged as a young research student from the Antipodes to begin work under Alfred Harker at Cambridge, and at a time when his interests were concentrated particularly on problems of metamorphism.

My own contributions in this field stem indeed from the stimulus I received then and through later years under his inspiring guidance.

Nor should I omit to mention at this time my debt to another great pioneer—George Barrow, who first directed my steps in the field of zonal metamorphism.

I treasure the friendships I have been privileged to enjoy with colleagues on this side of the Atlantic. If I should refer among these to one in particular of long standing, it is to that of Dr. Bowen. I recall the inspiring days—now almost thirty years ago—of participation in field excursions with Bowen and Harker in the glorious Isle of Skye, when the problems of monomineralic rocks, then a focus of Bowen's researches, were exemplified in the rusty peridotite dikes that climbed to the Cuillin sky.

Later came under his aegis, the opportunity of spending a period at the Geophysical Laboratory, a link that has remained precious through the years.

Would that I could feel that I had turned all these favours of fortune to the best account in the service of our Science.

Professor Buddington has been most kind in presenting my record, considering that he has had ample opportunity from personal experience, adequately to assess my deficiencies. His account does not hide from you that I am to be recognised as some sort of a hybrid of mixed mineralogical-petrological origin.

If then I should venture to add very shortly a few words on the prospect of some aspects of mineralogy, you would expect my appreciation to have been gleaned through petrological spectacles.

The present status of such subjects as granite, alkali rocks and the concept of nephelinization, peridotite and serpentine, carbonatite geology and metamorphic facies—to name but a few—presents an enthralling picture, and brings home to us that we live in stirring and romantic times.

Is it not already clear that to the solution of these challenging problems, experimental mineralogy has a great contribution to make? I see the prospect of mineralogy bright indeed.

Twelve years ago Professor Buddington in an address to the New York Mineralogical Club expressed the view that at least one new section of mineralogical science might be expected to develop on the average every ten years.

With the development of new experimental methods in the investigation of hydrous silicate systems, I believe such a new era in genetic mineralogy has arrived—may I call it the era of the conquest of the wet mineral silicate and the exploration of the subsolidus?

If I were to attempt to date its effective arrival, I should place it in 1949—ushered in with Bowen and Tuttle's experimental study of the system magnesia-silica-water, shedding new light yet posing new problems on the peridotite-serpentine enigma.

Our new era has already revealed something of the complexity of apparent simplicity among the great group of rock formers—the feldspars; yet in this field as each forward step is taken fresh problems loom ahead.

A new glow is emerging from the subsolidus of the nepheline system, and what prospects are in store for carbonatite geology and indeed carbonate rock metamorphism, when silicate systems bearing carbon dioxide surrender to quantitative treatment in the hydrothermal bomb?

I should not hazard a guess how soon an adequate body of data will be assembled and developed on such topics.

How true are the words of Faraday that it is the great beauty of science that advancement in it, whether in a degree great or small, instead of exhausting the subject of research, opens the door to further and more abundant knowledge, overflowing with beauty and utility.

So it is Mr. President that I foresee in our new experimental era, genetic mineralogy flourishing abundantly, opening the door to new vistas and playing a noble role in the elucidation of petrology's intractable systems.

Granted a few only by participation can hope to capture the supreme exhilaration of the chase, there remains for some the opportunity—though it may be inadequately seized—to play a part in applying the results of experimental disciplines—wet or dry—to the interpretation of their own petrological problems.

Though I have myself striven along these humbler lines, it is, I judge, more by persistence of effort than real achievement that I can in any way be considered to merit the honour you have conferred upon me.

It is therefore Mr. President, in a spirit of humility that I tender to the Mineralogical Society of America, my warmest thanks for the high compliment they have extended to me today.

PRESENTATION OF THE MINERALOGICAL SOCIETY
OF AMERICA AWARD TO HATTEN S. YODER, JR.*

J. F. SCHAIRER, *Geophysical Laboratory, Carnegie Institution of
Washington, Washington, D. C.*

Mr. President, Fellows and Members of the Mineralogical Society of America, and Guests:

My task on this occasion is a pleasure and privilege. I take great pride in introducing to you my colleague on the scientific staff of the Geophysical Laboratory and warm personal friend, Hatten S. Yoder, Jr.

The Geophysical Laboratory is a wonderful place to work, with all the advantages of good equipment, freedom from petty administrative responsibilities, and the inspiration that comes from working with a group of physicists, chemists, and geologists with a keen and lively interest in the nature of minerals and rocks and the mechanism of geological processes. As the years slip away we who were youngsters some years back begin to show our age by looking into the past as well as forward. The oldsters are prone to say that the world is slipping and things are not as they were in the "good old days." I remember those good old days when I first came down from Yale to the Geophysical Laboratory. What exciting days they were, with the contagious enthusiasm of such a brilliant group as Day, Allen, Washington, Bowen, Fenner, Wright, Merwin, Morey, Zies, Adams, Gibson, Greig, Posnjak, Tunell, Barth and others, and foreign visitors such as Eskola and Tilley! I am happy that I can say today that though many of the old group have now retired we still have today at the Geophysical Laboratory that same spirit of search and adventure in the complex realm of the physics and chemistry of geological processes with a young group every bit as able as the older generation.

We have one of this young group with us today and meet together here to do him honor. He has been chosen because of an outstanding paper on $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ in the Bowen Volume of the *American Journal of Science* (1952, pp. 569-627). I will let him tell you about his work and plans. He shows every promise of making many more brilliant contributions during the coming years to increase our imperfect knowledge of igneous and metamorphic processes.

Mr. President, I take great pleasure in presenting Dr. Hatten S. Yoder, Jr., for the Fourth Mineralogical Society of America Award.

* Yoder, Dr. Hatten Schuyler, Jr., Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C. Born in Cleveland, Ohio, March 20, 1921. A.A. 1940, B.S. (Geology) 1941, C.P.P.M. (Meteorology) 1942, Univ. Chicago; Ph.D. (Petrology) 1948, Mass. Inst. Tech. Lt. Comdr., U.S.N.R. (Aerology) 1942-1946. Navy Expedition to Siberia, 1945-1946. Fellow 1948, Petrologist 1949- , Geophysical Laboratory. Geol. Soc. Am., Am. Geophys. Union, Mineral. Soc. Am., Mineral. Soc. London, Geol. Soc. Finland, Am. Chem. Soc. Columbia Univ. Bicentennial Medal, 1954. Experimental petrology, phase equilibria in mineral systems; piezochemistry, properties of minerals at high pressures and high temperatures.

ACCEPTANCE OF THE MINERALOGICAL SOCIETY OF AMERICA AWARD

HATTEN S. YODER, JR., *Geophysical Laboratory, Carnegie
Institution of Washington, Washington, D. C.*

Mr. President, Dr. Schairer, Ladies, and Gentlemen:

It is with great personal pleasure that I accept the Mineralogical Society of America Award as representative of the Geophysical Laboratory. Few young men have had the exceptional opportunities that have been afforded me at the Geophysical Laboratory, and I am constantly aware of the fact that others given the same opportunities might have achieved far more important results. I have been surrounded by distinguished scientists willing to give counsel, provided with all the necessary experimental equipment, availed of liberal grants for field work and travel, given complete freedom from divergent duties, and assisted by outstanding, enthusiastic coworkers—all these advantages would cause anyone to accept such an honor *personally* with reluctance and humility. It should be clear that the published works on which this award is judged represent the cumulative effort of the Geophysical Laboratory. I hope you will forgive me if I cherish a small part of this award as my own.

I would like to take this opportunity to tell you of the thread which connects my various projects and publications. The main objectives of my research are, first, the quantitative evaluation of the grades of metamorphism and, second, an understanding of the origin of basalt. The $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ paper, for which the award is given, was aimed at the synthesis and stability range of chlorite and cordierite, two major constituents of the metamorphic rocks. Next the micas were tackled and the results of that work were presented in part last year with my colleague Hans Eugster. Yesterday you may have heard of the successful studies on the common garnet. Now it will be possible to measure the pressures and temperatures of the reactions marking some of the isograds.

While these steps are being taken, I am also working on the basalt problem. First, it was necessary to measure the melting points of minerals under pressure. In the course of the development of the apparatus for these extreme conditions, the α - β quartz transition was studied up to 10,000 bars. Then the apparatus was given a real trial on the change of melting point of diopside under pressure. This was followed by investigation of the diopside-water, anorthite-water and albite-water systems. Recently I have put some of these data to use in determining the



HATTEN S. YODER, JR.

Recipient of the Mineralogical Society of America Award

system anorthite-diopside-forsterite-water, which closely approaches the mineralogy of a basalt. Under way is work on the system albite-anorthite-water, also critical to the basalts.

In all these experiments water is an important constituent. An analysis of the role water plays in metamorphism was presented at the recent Columbia University Symposium on the Crust of the Earth. Some accused me of employing thirsty rock worms. Others described the water deficient region as Yoder's leaky umbrella. Of course, there were those blunt scholars who thought I was in the excess water region — "all wet." For these reasons, I encourage you to study carefully the critical role of water in metamorphism and other processes.

Again I would like to thank the Society for bestowing this honor upon me and I will endeavor to fulfill its purposes.

PROCEEDINGS OF THE THIRTY-FIFTH ANNUAL MEETING OF THE MINERALOGICAL SOCIETY OF AMERICA AT LOS ANGELES, CALIFORNIA

C. S. HURLBUT, JR., *Secretary*.

The thirty-fifth annual meeting of the Society held on November 1-3, 1954, at the Statler and Biltmore Hotels, Los Angeles, California, was attended by 185 fellows and members. Six scientific sessions were held, at which 63 papers were presented orally and 8 by title.

The annual luncheon of the Society held at the Biltmore Hotel on November 2d was attended by 152 fellows, members and guests. Following the luncheon the thirteenth presentation of the Roebling Medal was made to Cecil E. Tilley and the fourth presentation of the Mineralogical Society of America Award was made to Hatten S. Yoder, Jr.

Before the business meeting on the afternoon of November 2d the Society was addressed by the Retiring President, Sterling B. Hendricks, on *Polytypism and Screw Dislocation. An Appreciation of the Work on Crystal Growth of S. Amelinckx and W. Dekeyser*.

The 1954 Council of the Society met for seven hours on October 31st and discussed 25 items of business. The 1955 Council met for three hours on November 3d.

Of grave concern to the Council is the large backlog of manuscripts of papers held by the Editor to be published in *The American Mineralogist*. At the time of the meeting the Editor reported that he had on hand enough manuscripts for five issues of *The American Mineralogist* for 1955. With the May-June issue devoted to *Contributions to Canadian Mineralogy*, over a year elapses between the time of the receipt of a manuscript and the time of its publication. In order to have more space for scientific papers, the Council voted that beginning in 1956 the publication of abstracts of papers presented at the annual meeting will be discontinued. For the same reason the Council voted to publish the list of fellows and members only every other year.

During the past few years the Mineralogical Society of America has printed its own program for the annual meeting with abstracts of papers to be presented there. The general program printed by the Geological Society of America duplicates this material. As an economy measure, the Council voted to discontinue printing a separate program beginning in 1955 so that more money will be available for the publication of scientific papers. The program of the Geological Society of America will be sent to all fellows and members. The titles of papers presented at the annual meeting will be printed in the March-April issue of *The American Mineralogist* and reference will be given to the Bulletin of the Geological Society of America, where the abstracts may be found.

COMMITTEES OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1955

Financial Advisory Committee

E. P. Henderson, *Chairman* '54-'55
J. P. Marble '54-'55
R. E. Fuller '54-'56

Auditing Committee

H. F. McMurdie, *Chairman*
J. C. Rabbitt
C. L. Christ

Nominating Committee for Officers

W. T. Pecora, *Chairman*
V. T. Allen
A. Pabst
J. Gruner
J. S. Stevenson

Nominating Committee for Fellows

- R. B. Ferguson, *Chairman* '55
 J. T. Lonsdale '55
 T. F. Bates '55-'56
 J. J. Runner '55-'56
 A. E. J. Engel '55-'57
 R. J. Holmes '55-'57

Roebing Medal Committee

- L. G. Berry, *Chairman*
 G. Tunell
 M. Fleischer

Mineralogical Society of America Award Committee

- H. W. Fairbairn, *Chairman*
 J. J. Glass
 R. H. Jahns
 T. S. Lovering
 D. McConnell

Nomenclature Committee

- G. T. Faust, *Chairman* '55-'56
 A. L. Howland '55
 E. W. Nuffield '55
 G. Tunell '55-'56
 C. O. Hutton '55-'57
 E. E. Wahlstrom '55-'57

Publications Committee

- O. F. Tuttle, *Chairman* '55-'56
 N. L. Bowen '55-'56
 A. Pabst '55
 F. A. Bannister '55
 L. S. Ramsdell '55-'57
 R. S. Cannon '55-'57

Board of Associate Editors

- A. Pabst, *Chairman* '55
 E. F. Osborn '55
 Ian Campbell '55-'56
 Brian Mason '55-'56
 W. F. Bradley '55-'57
 F. J. Turner '55-'57

*Representatives**National Research Council*

- J. D. H. Donriay

American Geological Institute

- E. Ingerson '55
 A. Montgomery '55-'56

American Association for Advancement of Science

- A. Knopf

REPORT OF THE SECRETARY

To the Council of the Mineralogical Society of America:

ELECTION OF OFFICERS AND FELLOWS

Four hundred and sixty-eight ballots were cast in the election of officers, 163 by fellows and 305 by members of the Society. The officers elected to serve in 1955 are:

President: Harry H. Hess, Princeton University, Princeton, New Jersey.

Vice-President: Clifford Frondel, Harvard University, Cambridge, Massachusetts.

Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge, Massachusetts.

Treasurer: Earl Ingerson, U. S. Geological Survey, Washington, D. C.

Editor: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

Councilor (1955-58): Leonard G. Berry, Queen's University, Kingston, Ontario, Canada.

According to the provisions of the Constitution, the following have been elected to fellowship:

Stuart Olaf Agrell, Department of Mineralogy and Petrology, Cambridge, England.

Edgar H. Bailey, U. S. Geological Survey, Washington, D. C.

Robert M. Garrels, U. S. Geological Survey, Washington, D. C.

Hisashi Kuno, Tokyo University, Tokyo, Japan.

Fritz Laves, University of Chicago, Chicago, Illinois.

William Nunn Lipscomb, University of Minnesota, Minneapolis, Minnesota.

Charles Meyer, University of California, Berkeley, California.

John Drew Ridge, The Pennsylvania State College, State College, Pennsylvania.
 Edwin C. Roedder, University of Utah, Salt Lake City, Utah.
 Ogden Linne Tweto, U. S. Geological Survey, Denver, Colorado.

CHANGE IN THE CONSTITUTION

On the recent ballot, fellows were asked to vote on the following proposed change in Article III, Section 1 of the Constitution (deletions are indicated by brackets and additions by italics):

The officers of the Society shall be a president, a vice-president, a treasurer, a secretary, and an editor, who shall be elected annually. There shall be an executive council consisting of the above officers, the retiring president and [four] fellows at large, *two* to be elected each year for terms of [four] *three* years each.

This change was approved by a vote of 149 in the affirmative with 3 in the negative.

MEMBERSHIP STATISTICS

November 1, 1954

	1953	1954	Gain	Loss
Correspondents.....	4	4	0	0
Fellows.....	326	329	10	7
Members.....	857	931	149	75
Subscribers.....	856	934	136	58
	2043	2198	295	140

The above figures show a net gain of 3 fellows, 74 members and 78 subscribers. Considering the four groups together, there is a gain of 155, giving a total of 2198.

The Society lost through death four fellows: Lawson H. Bauer of the New Jersey Zinc Company, Franklin, New Jersey; Alton Gabriel of the Bureau of Mines, University, Alabama; A. C. Hawkins of Plainfield, New Jersey; and M. Vonsen of Petaluma, California.

Respectfully submitted,
 C. S. HURLBUT, JR., *Secretary*

REPORT OF THE TREASURER FOR 1954

To the Council of the Mineralogical Society of America:

Your Treasurer submits herewith his report for the fiscal year beginning August 1, 1953, and ending July 31, 1954.

RECEIPTS

Dues and subscriptions.....	\$ 9,121.51
Sale of back numbers.....	832.17
Authors' charges on reprints.....	2,251.86
Interest and dividends from endowment.....	4,484.60
Geological Society of America aid for printing the Journal.....	8,464.14
Advertising.....	1,353.69
Sale of Index, volumes 21-30.....	18.80
Sale of Index, volumes 1-20.....	5.80
Aid on expense of a long paper.....	270.00
National Science Foundation grant to aid printing a special issue.....	1,100.00
Contributions toward Ross-Schaller volume.....	627.84
	<hr/>
	\$28,530.41
Cash on hand, August 1, 1953.....	7,076.27
	<hr/>
	\$35,606.68

DISBURSEMENTS

Printing and distribution of the Journal (5 issues).....	\$17,400.44
Printing and distribution of reprints.....	1,407.31
Honorariums to Editor, Secretary, and Treasurer.....	1,062.50
Clerical Assistance.....	767.76
Postage and express.....	336.02
Printing and stationery.....	364.55
Office supplies and equipment.....	268.25
Program and abstracts (1953).....	681.85
Roebbling Medal.....	141.90
New securities purchased.....	952.00
Committee expenses.....	4.84
Expenses of officers to 1953 meetings.....	83.87
Safety deposit box.....	7.80
Refunds.....	47.07
Checks returned.....	27.48
Mineralogical Society of America Award certificate.....	7.50
Reprinting back issues in microtext.....	654.42
Pamphlet on mineralogy.....	30.25
Mineralogical Society of America luncheon.....	8.25
Dividend adjustment.....	7.88
Service charge on check.....	.25
	<hr/>
	\$25,062.10
Cash on hand, July 31, 1954.....	10,544.58
	<hr/>
	\$35,606.68

The endowment funds of the Society as of July 31, 1954, consist of the following securities:

BONDS

6M Atlantic Coast Line, 4½.....	\$5,257.50
5M New York Central, 5.....	4,300.00
5M Southern Railway, 5.....	5,743.75
	<hr/>
	\$15,301.25

PREFERRED STOCKS

200 Southern California Edison, 4.88.....	\$5,250.00
100 Union Pacific, 4.....	4,570.25
60 Jones and Laughlin, A, 5.....	4,987.50
55 United States Steel, 7.....	6,946.20
50 Virginia Electric and Power, 5.....	5,942.50
10 Consolidated Edison, 5.....	1,066.64
	<hr/>
	\$28,763.09

COMMON STOCKS

300 Potomac Electric Power.....	\$4,057.73
200 Greyhound Corporation.....	2,300.00
150 Spencer Kellogg.....	3,775.00
100 Columbus and Southern Ohio Electric.....	2,087.50
80 Kroger Co.....	1,990.00
60 United Fruit.....	3,067.50
56 Standard Oil of New Jersey.....	1,444.84

60 American Telephone and Telegraph.....	8,195.32	
50 Chesapeake and Ohio.....	2,368.75	
50 Phelps Dodge.....	1,975.00	
40 Plymouth Cordage.....	2,050.00	
30 U. S. Playing Card.....	2,411.25	
24 Public Service Electric and Gas.....	728.30	
		<hr/>
		\$36,451.29
		\$80,515.63

Respectfully submitted,
EARL INGERSON, *Treasurer*

DANA FUND

No disbursements were made during the fiscal year.

Available balance, July 31, 1954..... \$99.13

Respectfully submitted,
EARL INGERSON, *Treasurer*

REPORT OF THE AUDITING COMMITTEE

To the President of the Mineralogical Society of America:

The Auditing Committee has examined and verified the accounts of the Treasurer of the Mineralogical Society of America for the fiscal year beginning August 1, 1953, and ending July 31, 1954. The securities listed in the Treasurer's report, with all future coupons on the coupon bonds attached, are in the safety deposit box at the West End Branch of the Washington Loan and Trust Company in Washington, D. C.

Respectfully submitted,
WILLIAM L. HILL
HOWARD F. McMURDIE
J. J. FAHEY, *Chairman*

REPORT OF THE EDITOR FOR 1954

To the Council of the Mineralogical Society of America:

In presenting an editorial report for 1954 at this time, the same general procedure will be followed as in previous years. With five issues published and distributed and the November-December issue in galley form, sufficient data are now available to give a reasonably accurate general survey of the year's activity. When the editor's report appears in print in the March-April issue certain details incomplete and not available at the present time will be included so that the final printed report in April can be compared directly with those given in previous years.

In general, it may be stated that the accomplishments represent what might be termed the work of a good normal year with a volume of approximately 1050 pages. While this volume in size does not equal the one of last year that contained the exceedingly large November-December number dedicated to Ross and Schaller, still the 1954 volume may be regarded a very creditable accomplishment as each issue averaged about 175 pages.

By Council action one issue (May-June number) was set aside for "Contributions to Canadian Mineralogy." This policy begun in 1949 was continued in 1954 under the able editorship of Dr. L. G. Berry of Queen's University, Kingston, Ontario, and sponsored by the Walker Mineralogical Club. In this number the guest editor assembled 16 interesting papers on varied mineralogical subjects and assumed responsibility for their selection and

in seeing these contributions through the press. Aside from this single issue no other number was earmarked for a specific purpose.

The current volume as indicated will run about 1050 pages and contain 70 leading articles. Thirty-four additional short papers, appearing under Notes and News, give an overall total of 104 published manuscripts for the year. These contributions were received from 125 authors associated with 61 different universities, research bureaus and technical laboratories. Twenty-six critical book reviews, four new minerals described in detail for the first time and eighty-eight abstracts of new mineral names are a few of the other items of special mineralogical interest. One colored plate was employed to display the true color of the new mineral callaghanite.

As in previous years our service during 1954 has extended far beyond our own borders. During the current year 33 manuscripts (out of 104) came from 10 countries: Australia, Brazil, Canada, Denmark, England, Japan, Holland, Scotland, South Africa and Switzerland. These foreign contributions, although highly desirable in extending the influence of the Society's publication in distant lands, naturally reduce the space available and delay publication of American contributions.

As in the past the Geological Society of America has continued and increased its liberal financial support toward defraying a substantial portion of the printing costs of the Journal. For this assistance the Society is indeed very grateful and expresses its deep appreciation.

TABLE 1. DISTRIBUTION OF SUBJECT MATTER IN VOLUME 39

Subjects	Articles	Pages	Per Cent of Total
Leading articles*			
Descriptive mineralogy and paragenesis.	6		
Chemical mineralogy and geochemistry.	21		
Structural crystallography.	25		
Petrography.	7		
Memorials.	4		
Geometrical crystallography.	2		
Miscellaneous.	5		
	70	818	78.7
Shorter articles.	34	81½	21.3
Notes and news.	36	9½	
Proceedings of societies.	5	85	
Book reviews.	26	25½	
Abstracts of new mineral names.	88	20½	
Total entries.	259	1040	100.0
Illustrations.	235		
Index, Title Page, Table of Contents.		24	
Grand total.		1064	

* Leading articles averaged 11.7 printed pages each.

Respectfully submitted,
WALTER F. HUNT, *Editor*

And finally a word as to the prospects for 1955. The January-February manuscripts containing 10 main articles and 5 shorter contributions are in the hands of the printer. In addition at the present writing there are on file 42 major and 24 shorter contributions, or a total of 66 papers aggregating about 900 typed pages; approximately enough for 4 issues, exclusive of the January-February number.

The accompanying Table 1 summarizes in more detail the distribution of subject matter in volume 39.

LIST OF FORMER OFFICERS AND MEETING PLACES

By recommendation of the Council, a complete list of past officers is printed in the proceedings of the annual meeting of the Society:

HONORARY PRESIDENTS

Edward S. Dana 1925-1935
Charles Palache 1949-1954
Edward H. Kraus 1955-

PRESIDENTS

1920 Edward H. Kraus
1921 Charles Palache
1922 Thomas L. Walker
1923 Edgar T. Wherry
1924 Henry S. Washington
1925 Arthur S. Eakle
1926 Waldemar T. Schaller
1927 Austin F. Rogers
1928 Esper S. Larsen
1929 Arthur L. Parsons
1930 Herbert E. Merwin
1931 Alexander H. Phillips
1932 Alexander N. Winchell
1933 Herbert P. Whitlock
1934 John W. Wolff
1935 Clarence S. Ross
1936 William S. Bayley
1937 Norman L. Bowen
1938 Ellis Thomson
1939 Max N. Short
1940 William F. Foshag
1941 Frederick E. Wright
1942 Arthur F. Buddington
1943 John F. Schairer
1944 R. C. Emmons
1945 Kenneth K. Landes
1946 Paul F. Kerr
1947 M. J. Buerger
1948 M. A. Peacock
1949 John W. Gruner
1950 George Tunell

1951 A. Pabst
1952 Michael Fleischer
1953 J. D. H. Donnay
1954 Sterling B. Hendricks

SECRETARIES

1920-1922 Herbert P. Whitlock
1923-1933 Frank R. Van Horn
1933-1934 Albert B. Peck
1934-1944 Paul F. Kerr
1944- C. S. Hurlbut, Jr.

VICE-PRESIDENTS

1920 Thomas L. Walker
1921 Waldemar T. Schaller
1922 Frederick A. Canfield
1923 George F. Kunz
1924 Washington A. Roebbing
1925 Herbert P. Whitlock
1926 George Vaux, Jr.
1927 George L. English
1928 Lazard Cahn
1929 Edward Wigglesworth
1930 John E. Wolff
1931 William F. Foshag
1932 Joseph L. Gillson
1933 Frank B. Guild
1934 William A. Tarr
1935 Ellis Thomson
1936 Harold L. Alling
1937 H. V. Ellsworth
1938 Kenneth K. Landes

1939 Burnham S. Colburn
 1940 Ian Campbell
 1941 William J. McCaughey
 1942 Martin J. Buerger
 1943 John W. Gruner
 1944 Harry Berman
 1945 George Tunell
 1946 S. B. Hendricks
 1947 Carl Tolman
 1948 Adolf Pabst
 1949 J. D. H. Donnay
 1950 Ralph E. Grim

1951 Michael Fleischer
 1952 J. D. H. Donnay
 1953 Sterling B. Hendricks
 1954 Harry H. Hess

TREASURERS

1920-1923 Albert B. Peck
 1924-1929 Alexander H. Phillips
 1929-1930 Albert B. Peck
 1930-1940 Waldemar T. Schaller
 1941- Earl Ingerson

EDITORS

1920-1921 Edgar T. Wherry 1922- Walter F. Hunt

COUNCILORS

1920 Arthur S. Eakle, Frank R. Van Horn, Fred E. Wright, Alexander H. Phillips.
 1921 Frank R. Van Horn, Fred E. Wright, Alexander H. Phillips, Austin F. Rogers.
 1922 Fred E. Wright, Alexander H. Phillips, Austin F. Rogers, Thomas L. Watson.
 1923 Alexander H. Phillips, Austin F. Rogers, Thomas L. Watson, Esper S. Larsen.
 1924 Austin F. Rogers, Thomas L. Watson, Esper S. Larsen, Arthur L. Parsons.
 1925 Thomas L. Watson, Esper S. Larsen, Arthur L. Parsons, William F. Foshag.
 1926 Esper S. Larsen, Arthur L. Parsons, William F. Foshag, William A. Tarr.
 1927 Arthur L. Parsons, William F. Foshag, William A. Tarr, Alexander N. Winchell.
 1928 William F. Foshag, William A. Tarr, Alexander N. Winchell, Ellis Thomson.
 1929 William A. Tarr, Alexander N. Winchell, Ellis Thomson, Clarence S. Ross.
 1930 Alexander N. Winchell, Ellis Thomson, Clarence S. Ross, Paul F. Kerr.
 1931 Ellis Thomson, Clarence S. Ross, Paul F. Kerr, William S. Bayley.
 1932 Clarence S. Ross, Paul F. Kerr, William S. Bayley, William J. McCaughey.
 1933 Paul F. Kerr, William S. Bayley, William J. McCaughey, Kenneth K. Landes.
 1934 William S. Bayley, William J. McCaughey, Kenneth K. Landes, E. P. Henderson.
 1935 William J. McCaughey, Kenneth K. Landes, E. P. Henderson, J. F. Schairer.
 1936 Kenneth K. Landes, E. P. Henderson, J. F. Schairer, Arthur F. Buddington.
 1937 E. P. Henderson, J. F. Schairer, Arthur F. Buddington, Arthur P. Honess.
 1938 J. F. Schairer, Arthur F. Buddington, Arthur P. Honess, R. C. Emmons.
 1939 Arthur F. Buddington, Arthur P. Honess, R. C. Emmons, Carl Tolman.
 1940 Arthur P. Honess, R. C. Emmons, Carl Tolman, D. Jerome Fisher.
 1941 R. C. Emmons, Carl Tolman, D. Jerome Fisher, Martin A. Peacock.
 1942 Carl Tolman, D. Jerome Fisher, Martin A. Peacock, Adolf Pabst.
 1943 D. Jerome Fisher, Martin A. Peacock, Adolf Pabst, C. S. Hurlbut, Jr.
 1944 Martin A. Peacock, Adolf Pabst, Michael Fleischer, S. J. Shand.
 1945 Adolf Pabst, Michael Fleischer, S. J. Shand, R. E. Grim.
 1946 Michael Fleischer, S. J. Shand, R. E. Grim, Joseph Murdoch.
 1947 S. J. Shand, R. E. Grim, Joseph Murdoch, H. H. Hess.
 1948 R. E. Grim, Joseph Murdoch, H. H. Hess, Clifford Frondel.
 1949 Joseph Murdoch, H. H. Hess, Clifford Frondel, Lewis S. Ramsdell.
 1950 H. H. Hess, Clifford Frondel, Lewis S. Ramsdell, E. F. Osborn.
 1951 Clifford Frondel, Lewis S. Ramsdell, E. F. Osborn, George T. Faust.
 1952 Lewis S. Ramsdell, E. F. Osborn, George T. Faust, Victor T. Allen

- 1953 E. F. Osborn, George T. Faust, Victor T. Allen, C. Osborne Hutton.
 1954 George T. Faust, Victor T. Allen, C. Osborne Hutton, Felix Chayes

ANNUAL MEETING PLACES

- | | |
|-------------------------------|-------------------------------|
| 1920 Chicago, Illinois | 1938 New York, N. Y. |
| 1921 Amherst, Massachusetts | 1939 Minneapolis, Minnesota |
| 1922 Ann Arbor, Michigan | 1940 Austin, Texas |
| 1923 Washington, D. C. | 1941 Boston, Massachusetts |
| 1924 Ithaca, New York | 1942 No meeting held |
| 1925 New Haven, Connecticut | 1943 No meeting held |
| 1926 Madison, Wisconsin | 1944 No meeting held |
| 1927 Cleveland, Ohio | 1945 Pittsburgh, Pennsylvania |
| 1928 New York, N. Y. | 1946 Chicago, Illinois |
| 1929 Washington, D. C. | 1947 Ottawa, Canada |
| 1930 Toronto, Canada | 1948 New York, N. Y. |
| 1931 Tulsa, Oklahoma | 1949 El Paso, Texas |
| 1932 Cambridge, Massachusetts | 1950 Washington, D. C. |
| 1933 Chicago, Illinois | 1951 Detroit, Michigan |
| 1934 Rochester, New York | 1952 Boston, Mass. |
| 1935 New York, N. Y. | 1953 Toronto, Canada |
| 1936 Cincinnati, Ohio | 1954 Los Angeles, California |
| 1937 Washington, D. C. | |

RECIPIENTS OF THE ROEBLING MEDAL

- | | |
|--------------------------------------|---------------------------------------|
| Charles Palache, December 1937 | William Lawrence Bragg, November 1948 |
| Waldemar T. Schaller, December 1938 | Herbert E. Merwin, November 1949 |
| Leonard James Spencer, December 1940 | Norman L. Bowen, November 1950 |
| Esper S. Larsen, Jr., December 1941 | Fred E. Wright, November 1952 |
| Edward H. Kraus, February 1945 | William F. Foshag, November 1953 |
| Clarence S. Ross, December 1946 | Cecil Edgar Tilley, November 1954 |
| Paul Niggli, December 1947 | |

RECIPIENTS OF THE MINERALOGICAL SOCIETY OF AMERICA AWARD

- | | |
|-------------------------------------|-------------------------------------|
| Orville Frank Tuttle, November 1951 | L. H. Ahrens, November 1953 |
| Frederick H. Stewart, November 1952 | Hatten S. Yoder, Jr., November 1954 |

ABSTRACTS OF PAPERS PRESENTED AT THE THIRTY-FIFTH ANNUAL MEETING OF THE MINERALOGICAL SOCIETY OF AMERICA, NOVEMBER 1-3, 1954

URANIUM IN APATITE*

Z. S. ALTSCHULER, R. S. CLARKE, JR., AND E. J. YOUNG

U. S. Geological Survey, Washington, D. C.

Apatite contains only traces of uranium, yet as apatite is a minor constituent in most rocks and the major constituent of a few very large deposits it accounts, paradoxically, for both dispersal and concentration of uranium in nature.

Uranium is typically 0.00X per cent of primary igneous apatite and 0.00X to 0.01X per cent of sedimentary marine apatite. End-stage igneous apatite may contain 0.0X per cent uranium. Analogously, marine reworked apatite becomes enriched in uranium from 0.00X to 0.0X per cent. This is demonstrated by the greater uranium contents of the texturally more complex phases within a single deposit.

Uranium can be secondarily leached from or introduced into apatite by ground water. These secondary changes are indicated by the existence of pronounced concentration gradients within single pebbles of apatite as well as by the redistribution of uranium among different mineral hosts in leached and altered sections of phosphorite.

It is proposed that uranium replaces calcium in the apatite structure. This is signified by several lines of investigation. Uranium and calcium contents parallel one another in sections of leached and altered phosphorite. Ionic radii of tetravalent uranium (1.05 \AA) and divalent calcium (1.06 \AA) are virtually identical, and most of the uranium in igneous, sedimentary, and bone apatite is found to be tetravalent. Petrographic and chemical analyses and nuclear emulsion studies have shown that uranium in apatite is disseminated rather than locally concentrated. In addition, phosphate deposits are essentially devoid of uranium minerals.

OCCURRENCE OF CHARNOKITE SERIES IN BUNGER LAKE AREA, ANTARCTICA

E. T. APFEL AND W. T. HUANG

Syracuse University, Syracuse, New York, and
University of Oklahoma, Norman, Oklahoma

The Bunger Lake area lying between $66^{\circ}7' \text{ S.}$ latitude and $100^{\circ}56' \text{ E.}$ longitude [of the Antarctica] covers approximately 30 by 15 miles.

The rocks collected represent a wide variety of Precambrian igneous and metamorphic types. The outstanding ones are represented by the charnockite series. The acid and intermediate members of the series consist of erratics which have no clear relation with the basic member. The basic member is found at the northern end of the area. Its geologic setting is known.

The charnockite series is represented by hypersthene granite, hypersthene tonalite, and members designated as norite and noritic charnockite, respectively. Contamination of some basic charnockites by granitic emanations provides a clue to the origin of the erratics in which hypersthene may have been derived from the basic charnockites.

The mineralogical features of petrogenic significance are: (1) the paucity of water in the charnockites is indicated by mineral species, (2) an increase in the FeO/MgO ratio as evidenced by the character of the hypersthene in the more acid charnockite is in accord with

* Publication authorized by the Director, U. S. Geological Survey.

the trend of crystallization in mafic magmas, (3) strong development of microperthites and myrmekite, (4) garnet occurs in hypersthene granite while augite is confined to noritic charnockites.

In view of the similarity of occurrence, mineralogy, chemical characters, and textural features of the Bunker Lake charnockites to those of other Antarctic charnockites, it appears that these rocks were originally a differentiated series of basic igneous intrusions, and have subsequently undergone metamorphism during a period of granitization. The discovery of the charnockites in this area has added a fourth distinct province to Antarctica.

PARTICLE SIZES OF CLAY MINERALS BY SMALL-ANGLE X-RAY SCATTERING

RONALD J. ARNOTT

The Texas Company Research Laboratory, Bellaire, Texas

A review of the present methods of particle size determination of clay minerals indicates that none are entirely adequate. Electron microscopy has provided the first reliable measure of clay sizes but gives poor results with montmorillonite and illite. This paper describes an investigation of small-angle x-ray scattering as a possible technique in the study of clay minerals. The interpretation used is that of Shull and Roess involving a graphical comparison of experimental scattering curves with theoretical scattering curves. In theory, both the distribution of particle sizes and the shape of the particles should be obtainable, but in practice outside evidence of the shape is required.

A two-crystal spectrometer was used to collect data for two carbon black samples and twenty-eight clay samples. The carbon blacks and most of the clays gave scattering curves from which particle size information could be extracted. The scattering curves for the halloysites and attapulgites could not be interpreted, probably because of their fibrous or tubular character. Of five purified samples of illite and montmorillonite, four gave uninterpretable scattering curves, possibly due to extreme orientation during treatment. Because of the scarcity of similar data in the literature it is difficult to verify the particle size information derived. However, it is believed that the small-angle x-ray scattering technique will fill the need for a relatively simple method of determining clay sizes.

MINERALOGY AND PETROGRAPHY OF THE CHATTANOOGA SHALE

T. F. BATES, E. O. STRAHL, N. M. SHORT, E. N. SILVERMAN, AND E. CAMILLI

Pennsylvania State University, State College, Pennsylvania

Detailed mineralogical and petrographic analysis of a drill core of the Chattanooga formation has resulted in a clearer picture of the relationship of uranium with the composition and texture of the black shale from the Highland Rim area of Tennessee.

Thin-section point counts, alpha-track counts and quantitative mineralogical and chemical analyses of sixty samples from thirty-five feet of core have yielded statistically significant correlations between uranium and some of the shale constituents. The correlation is positive with respect to "blackness" of the sample, total carbon, pyrite, and total sulfur, and negative with quartz, feldspar and clay and with Fe_2O_3 . The absence of high correlation coefficients indicates that the uranium is not specific to any single constituent that was measured. On the other hand certain relationships between uranium content and composition are apparent.

The upper member of the formation is darkest in color, shows the least mineralogical and petrographic variation and contains the highest concentration of uranium. The four lower members are more heterogeneous and consist of alternating gray and black beds. The gray beds are finer in grain size and contain more quartz, feldspar, and clay and less pyrite and organic matter than the black layers.

Autoradiographic studies demonstrate that the alpha particle source material is localized about concentrations of organic matter and pyrite.

X-RAY IDENTIFICATION OF CHLORITE SPECIES

G. W. BRINDLEY AND F. G. GILLERY

The Pennsylvania State University, State College, Pennsylvania

The identification of chlorites by x -rays has advantages over other methods for fine grained and impure materials. Since all chlorites have the same general structural scheme, and since particular species differ only in chemical composition, it is essential to consider the finer details of the x -ray pattern in any attempt to identify species by x -ray data alone. The principal isomorphous replacements are Al for Si in tetrahedral positions and Fe, Al . . . for Mg in octahedral positions. Simplifying assumptions reduce the problem for most chlorites to the determination of (1) the proportion of octahedral sites occupied by Fe, (2) the proportion of tetrahedral sites occupied by Al; i.e., two parameters are involved and these can be determined by consideration of (1) the intensities of the basal reflections, (2) the basal spacing. The use of the b lattice parameter is considered inadvisable. Examples are given of the identification of three chlorites by the x -ray method prior to chemical analysis. Subsequent chemical analysis showed that the x -ray data had given a reasonably accurate estimate of their compositions. While most chlorites are trioctahedral minerals, there is the possibility that dioctahedral types and mixed di-tri types may exist. Their recognition from x -ray data is considered. Some precautions which are necessary when measuring and interpreting basal intensities with a counter spectrometer are discussed.

CARBON 14 AGE RESEARCH

WALLACE BROECKER AND J. LAURENCE KULP

Lamont Geological Observatory (Columbia University), Palisades, New York

Recent developments at the Lamont Observatory have involved extension of the C^{14} age method to 45,000 years by the utilization of large volume acetylene proportional counters with consequent increase in precision for modern samples. New measurements of geological and archeological samples supply information on a number of current problems. The rate of rise in sea level in the Mississippi Delta region over the past 30-40,000 years has been studied by the aid of wood and shell material taken from cores. The rate appears to be about a foot per century. Both the Robson and Malaspina glaciers show evidence of advance followed by retreat during the past 500 years. Samples of peat from the James Bay area, Canada, suggest that the end of the continental glacier in that area occurred only some 3,000 years ago.

Fossil organic muck appears to give reliable ages which agree with wood in the same horizon. The first dates from the Neolithic archeological sites in southeastern China (HongKong area) indicate 3,000 years. The alleged Norse ship at Follins Pond, Mass., is found to be from the Colonial period. A layer of dirt several feet from the surface of one of the ice islands shows an apparent age of less than 500 years, indicating relatively rapid accumulation. A "sea biscuit" from the top of the Atlantic seamount shows an age of 12,000 years. These and other results will be interpreted in terms of their geological significance.

RELATIONSHIP BETWEEN DENSITY AND COMPOSITION IN THE COLUMBITE-TANTALITE SERIES

WILLIAM J. CAMPBELL AND JOHN G. PARKER

U. S. Bureau of Mines, College Park, Maryland

A study was undertaken to determine if the Nb_2O_5/Ta_2O_5 ratio in members of the

columbite-tantalite series could be evaluated from the relationship of density to composition.

A number of samples in this series were analyzed by means of fluorescent x-ray spectrography. The samples were checked by x-ray diffraction on a wide range goniometer. Densities were measured with a precision of ± 0.02 by application of a double pycnometer technique.

The theoretical relationship between density and $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ ratio indicates that density is a linear function of the atomic per cent Ta_2O_5 . The x-ray diffraction studies show a small decrease in unit cell size with increasing FeO/MnO ratio but independent of the $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ ratio. The following equation was obtained:

$$\rho = (A + B \text{ atomic } \% \text{ Ta}_2\text{O}_5)(1 + C \text{ atomic } \% \text{ FeO})$$

in which A, B, and C are empirically determined constants.

It is concluded that application of the above expression permits evaluation of the $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ ratio with an accuracy equal to that obtained by conventional chemical techniques.

CONTEMPORANEOUS SLUMPING AND SLIDING IN THE BANDED GABBROS OF THE ISLE OF SKYE, SCOTLAND

J. M. CARR

University of Illinois, Urbana, Illinois

Structures attributed to slumping and sliding of stratified crystal-mush occasionally affect gabbroic rocks at the heart of the Cuillin complex. The rocks are at differing horizons of a Skaergaard-type layered series that formed by the bottom accumulation of discrete crystals on inclined surfaces. The observed dip of undisturbed layers varies between 35° and 50° . Blocky xenoliths of layered gabbro have been emplaced by gravity-sliding over the sloping surface of the parent-layer, sometimes with the formation of a slide-breccia. Lack of disturbance in overlying layers indicates that sliding occurred whilst the host-layer was still accumulating. Fracturing and separation of blocks was generally confined to layers which possessed an igneous lamination. Accompanying massive-textured layers, formed of mush with a greater liquid content, have flowed rather than fractured. The variable fluidity of the interlayered mush seems to explain earlier erroneous views on the age-relations of the Cuillin banded gabbros. The preponderant stability of the unconsolidated material, which was often deposited on slopes excessively steep by subaqueous standards, is attributed chiefly to the high viscosity possessed by magma.

PRECISION DETERMINATION OF LATTICE CONSTANTS OF SINGLE CRYSTALS USING THE CONVENTIONAL WEISSENBERG CAMERA

C. L. CHRIST

U. S. Geological Survey, Washington, D. C.

The well-known graphical extrapolation method of Bradley and Jay [*Proc. Phys. Soc.*, 44, 563 (1932)] is a very powerful means of obtaining precise lattice constants of crystals. However, to apply this method it is necessary that the spacing data derived from film measurements be relatively free from errors due to film shrinkage and incomplete knowledge of the camera radius. In the present method a powder pattern of finely divided, annealed silver is recorded on the Weissenberg pattern of the crystal under study. From measurements of the silver pattern a film constant as a function of 2θ is derived. This is used to convert linear measurements of the Weissenberg spots to the corresponding 2θ values. With a conventional Weissenberg camera and a relatively crude commercial measuring device a precision of lattice constant of 3 to 4 parts in 10,000 may be obtained routinely from a single crystal.

CRYSTAL STRUCTURE OF COLEMANITE, $\text{CaB}_2\text{O}_7(\text{OH}) \cdot \text{H}_2\text{O}$

C. L. CHRIST, JOAN R. CLARK, AND H. T. EVANS, JR.

U. S. Geological Survey, Washington, D. C.

Colemanite is monoclinic $P2_1/a$, $a = 8.743 \pm 0.004$, $b = 11.264 \pm 0.002$, $c = 6.102 \pm 0.003$ Å, $\beta = 110^\circ 07' \pm 05'$, $Z = 4$ [Christ, *Am. Mineral.*, 38, 411 (1953).]

From extensive 3-dimensional intensity data the phases of 944 observed structure amplitudes were calculated by the method of Hauptman and Karle (ACA Monograph #3, The Letter Press, Wilmington, Del., 1953). These results were used to calculate electron density sections over the xz plane at intervals along y of $1/60$, for $y=0$ to $y=\frac{1}{2}$. Analysis of the electron-density sections shows that there are infinite boron-oxygen chains running parallel to the a -axis. The chain element has the composition $[\text{B}_2\text{O}_4(\text{OH})_3]^{-2}$ and consists of a BO_3 triangle and two BO_4 tetrahedra. The average B-O bond length in the tetrahedra is 1.43 and in the triangle is 1.37 Å. Ca^{++} has as nearest neighbors 5 oxygens and 1 water molecule at an average distance of 2.41 Å. The structure is being refined at the present time.

APPLICATION OF ELECTRON DIFFRACTION TO THE STUDY OF METAMICT MINERALS

C. L. CHRIST, E. J. DWORNIK, AND M. S. TISCHLER

U. S. Geological Survey, Washington, D. C.

Metamict minerals, whose structures have been distorted by bombardment by the emanations from radioactive elements, yield poor or no x-ray diffraction patterns and optically are birefringent or isotropic. It has been found that at least some of these metamict minerals give sharp electron diffraction patterns. Apparently, sufficient relict crystallinity is retained so that the relatively short wavelength electrons ($\lambda = 0.055$ Å at 50 KV) will yield resolved patterns.

Electron diffraction studies have been started on various metamict minerals. Zoned zircon from Oklahoma was examined and both fresh and highly metamict portions of a given zircon yielded numerous diffraction rings. X-ray diffraction patterns of these same samples were sharp and with measurable lines in the case of fresh zircon, but they were poor and with no measurable lines in the case of the metamict zircon. Similarly, good electron diffraction patterns of metamict samarskite and pyrochlore have been obtained.

OPTICAL AND CHEMICAL STUDY OF JADEITE FROM CALIFORNIA

ROBERT G. COLEMAN

U. S. Geological Survey, Washington, D. C.

The green to white jadeite from Clear Creek, San Benito County, California, described by Chesterman and Yoder, has been further investigated as part of a mineralogic and petrologic study of the New Idria district. The jadeite is found in small veins cutting albite-glaucophane-acmite schist and as larger lens-shaped pods within serpentine. The vein jadeite is associated with albite, analcime, natrolite, and thomsonite. Prehnite, hydrogrossular, thomsonite, and minor sphene are found associated with the jadeite pods. A chemical analysis, in per cent, shows the white vein material to be almost pure jadeite: SiO_2 59.38, Al_2O_3 25.82, FeO traces, Fe_2O_3 0.45, TiO_2 0.04, NaO 0.13, MgO 0.12, K_2O 0.02, Na_2O 13.40, $\text{H}_2\text{O}+$ 0.22, $\text{H}_2\text{O}-$ 0.16, Cr_2O_3 0.01, total 99.75. Optical data: $\alpha = 1.654$, $\beta = 1.657$, $\gamma = 1.666$, $\gamma - \alpha = 0.012$, $2V = 70^\circ \pm$, $Z \wedge c = 34^\circ$, $X = Z = Y$ colorless. Density: 3.43 ± 0.01 . Chemical analysis of the green jadeite shows that it carries about 10 per cent of the diopside molecule and 14 per cent of the acmite molecule. The mineral association suggests that the jadeite has formed under low temperature and pressure conditions, and that there are several possible modes of origin.

ISOTOPIC GEOCHEMISTRY OF THERMAL WATERS

HARMON CRAIG, GIOVANNI BOATO,* AND DONALD E. WHITE

Institute for Nuclear Studies, University of Chicago; U. S. Geological Survey,
Menlo Park, California

The relationships between volcanic and hot spring waters and local meteoric waters are being studied by "natural" isotopic tracer techniques utilizing both deuterium and oxygen 18. The isotopic "labelling" is provided by multiple stage fractional distillation processes over the oceans which produce large variations in the isotopic composition of meteoric waters in different regions of the earth. Thermal waters in areas of widely different surface water composition are then studied in detail for seasonal variations in isotopic and chemical composition.

The lightest thermal waters so far encountered occur at Yellowstone Park, while the heaviest occur in New Zealand; these differences are matched by the meteoric waters. The thermal waters in these localities differ in deuterium and oxygen 18 content by as much as 20% and 3% respectively, yet the isotopic relationships between surface waters, alkaline hot springs, and acid springs are the same in these and in areas of intermediate meteoric water composition. These relationships, correlated with experimental evidence, show that the acid hot springs in all areas examined are of secondary origin, derived from near-neutral and alkaline ground waters by non-equilibrium evaporation—condensation processes in which the waters become enriched in the heavy isotopes and in sulfuric acid. The alkaline springs are of direct meteoric origin; small amounts of juvenile or "recycled" water may be present and detailed studies are being made on the maximum percentages of these constituents.

CRYSTAL STRUCTURE OF SANBORNITE, BaSi_2O_6

ROBERT M. DOUGLASS

University of California, Berkeley, California

Sanbornite, previously described as triclinic, is apparently orthorhombic; space group P_{cmn} . The unit cell, $a=4.63$, $b=7.69$, $c=13.53$ Å, contains $4\text{BaSi}_2\text{O}_6$.

A structure with thirteen parameters has been found with the aid of Patterson and Fourier projections. It is a silicate sheet structure with two parallel, identical $\text{Si}_4\text{O}_{10}^{4-}$ sheets per unit cell lying in x , y , $\frac{1}{4}$ and x , y , $\frac{3}{4}$, and two Ba^{+2} lying roughly half way between each successive pair of sheets. Each $\text{Si}_4\text{O}_{10}^{4-}$ sheet may be regarded as made up of continuously linked, distorted six-membered rings of SiO_4 tetrahedra. The tetrahedra are arranged in pairs, one tetrahedron lying on either side of the m plane in x , $\frac{1}{4}$, z or x , $\frac{3}{4}$, z . Pairs of tetrahedra within one sheet are related by glide reflection on the n plane in x , y , $\frac{1}{4}$ or x , y , $\frac{3}{4}$, so that unshared vertices of alternate pairs point up, the others down. Each sheet is derivable from the other by glide reflection on the c plane in $\frac{1}{2}$, y , z or $\frac{3}{2}$, y , z . Each barium atom is surrounded by seven nearest oxygen atoms.

STUDIES IN THE URANIUM-LEAD METHOD OF AGE DETERMINATION

W. R. ECKELMANN AND J. L. KULP

Lamont Geological Observatory (Columbia University), Palisades, New York

During the past year several dozen complete age analyses have been made on samples of pitchblende, uraninites and samarskites from a number of important localities. Isotopic

* Present address: Istituto di Fisica Sperimentale dell'Università, Genova, Italy.

ratios of $\text{Pb}^{206}/\text{U}^{238}$, $\text{Pb}^{207}/\text{U}^{235}$, $\text{Pb}^{206}/\text{Pb}^{210}$, $\text{Pb}^{208}/\text{Th}^{232}$ and $\text{Pb}^{207}/\text{Pb}^{206}$ have been obtained for all samples where concentrations permitted. Radon leakage has been measured and corrected for as well as the common lead contamination. Several localities which have had age determinations made previously are included for comparison. Wilberforce, Ontario, remains at about 1040 m.y., Gilpin Co., Colo. at 50–60 m.y., and the Besner Mine, Ont., at about 820 m.y. New values include the Spruce Pine, N. C., pegmatite district at about 320 m.y., Joachimsthal at about 200 m.y., and Baden, Germany, at about 110 m.y.

A large number of pitchblende samples from the Lake Athabasca region were analyzed chemically and isotopically. Apparent ages from the various isotopic ratios differ considerably. It appears possible to interpret these results in terms of radon leakage, the preferential leaching of lead during recent geologic time, and several periods of pitchblende deposition or redeposition. The oldest pegmatite deposit in the area appears to be about 1700 m.y. The oldest pitchblende which has not been subjected to later chemical effects appears to be about 1670 m.y. More recent deposition or redeposition appears at approximately 350 m.y. The data include apparent ages from specimens taken from the same level, from different levels of the same mine, and from several widely separated mines in the Athabasca district.

STABILITY AND OCCURRENCE OF PARAGONITE

H. P. EUGSTER AND H. S. YODER

Geophysical Laboratory, Washington, D. C.

Two modifications of paragonite have been synthesized: a 1-layer monoclinic (1M) and a two-layer monoclinic (2M) form. The univariant curve for the reaction $\text{paragonite} \rightleftharpoons \text{albite} + 2 \text{ corundum} + 2 \text{ water}$ passes through the points 660° C.–30,000 psi water vapor pressure, 625° C.–15,000 psi, 610° C.–10,000 psi and 580° C.–5,000 psi. The point for 1 atm. was calculated and found to be 395° C.

The two forms can readily be distinguished in powder x-ray diffraction patterns. At temperatures above 400° C. the 2M paragonite is the more stable form. All natural paragonites studied so far show a powder pattern identical with the 2M form.

X-ray studies of many natural paragonites showed that in mica schists paragonites are usually accompanied by muscovite. In these cases the powder patterns are those of mechanical mixtures of the two micas and suggest that the solid solution between muscovite and paragonite is limited. The c_0 for synthetic paragonite is 19.27 Å, and for natural paragonites an extrapolation to the end member gives $c_0 = 19.15$ Å. The maximum displacement of the basal spacing for a natural paragonite associated with muscovite was found to be 22% of the total difference between paragonite and muscovite.

Of 90 mica-bearing schists from the Lincoln Mtn. and Hyde Park Quadrangles (Vt.) 33 samples contained paragonite in amounts up to 60% of the total mica content. Paragonite mainly appears in albite-free assemblages with kyanite, chloritoid, or chlorite. Staining for potassium was helpful in distinguishing paragonite from muscovite in thin sections.

CONSTITUTION OF THE NATURAL AND ARTIFICIAL DECAVANADATES

HOWARD T. EVANS, JR., MARY E. MROSE AND R. MARVIN

U. S. Geological Survey, Washington, D. C.

When an alkaline solution of V_2O_5 is brought to a pH of about 6.5, it suddenly turns orange, and when concentrated, yields a variety of crystalline products. These products are very similar to the minerals, pascoite and hummerite, which are leached out of the vanadium oxide ores in the Colorado Plateaus area by surface waters. New x-ray data have

been accumulated which relates these minerals to the artificial system and throws light on their basic constitution. All data were measured on artificial crystals.

- (I) $K_6V_{10}O_{28} \cdot 10H_2O$: triclinic, space group, $P\bar{1}$ (pseudo-monoclinic, $I2/m$), $a=17.78 \text{ \AA}$, $b=11.28$, $c=17.48$, $\beta=130^\circ 15'$, $Z=4$.
- (II) $K_6V_{10}O_{28} \cdot 10H_2O$: monoclinic, space group, $P2_1/n$, $a=18.34 \text{ \AA}$, $b=17.42$, $c=10.56$, $\beta=94^\circ 20'$, $Z=4$.
- (III) $Ca_3V_{10}O_{28} \cdot 16H_2O$ (pascoite): monoclinic, space group $C2/M$, $a=16.89 \text{ \AA}$, $b=10.20$, $c=10.91$, $\beta=93^\circ 20'$, $Z=2$.
- (IV) $K_2Mg_2V_{10}O_{28} \cdot 16H_2O$ (hummerite; see A. D. Weeks, E. A. Cisney and A. M. Sherwood, *Am. Min.*, 36, 326, 1951): triclinic space group $P\bar{1}$, $a=10.81 \text{ \AA}$, $b=11.01$, $c=8.85$, $\alpha=106^\circ 04'$, $\beta=107^\circ 49'$, $\gamma=65^\circ 40'$, $Z=1$.
- (V) $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$: triclinic, space group $P\bar{1}$, $a=10.76 \text{ \AA}$, $b=11.17$, $c=8.77$, $\alpha=104^\circ 50'$, $\beta=109^\circ 29'$, $\gamma=65^\circ 05'$, $Z=1$.

The crystal structure analysis of IV and V is in progress.

CONCENTRATION OF HEAVY ACCESSORIES FROM LARGE ROCK SAMPLES

H. W. FAIRBAIRN

Massachusetts Institute of Technology, Cambridge, Massachusetts

Concentration of heavy accessories from large rock samples (circa 50 lb.) requires, in the interest of efficiency, some modification of standard techniques currently used for small samples. The Carpcu induced roll separator will remove the magnetic fraction. The non-magnetic residue is then passed through a continuous flow heavy-liquid separator which reduces handling and economizes on time. It consists of an assembly of two stainless steel beakers mounted above one another. The upper beaker contains a thin, thoroughly mixed sludge of heavy liquid and sized sand. This is fed slowly through a conical valve into the beaker underneath, where fractionation into float and sink occurs. The float is continuously removed by a jiggling device and the sink is collected after completion of the run. An improved method of washing the float consists of adding water to the sand after removal of the excess heavy liquid. This gives much greater recovery of undiluted heavy liquid than is otherwise possible and reduces the volume of diluted acetone washings which comprises the final stage.

DIFFERENTIATION TRENDS IN THE LORING INTRUSIVES OF CANADA

GERALD M. FRIEDMAN

University of Cincinnati, Cincinnati, Ohio

Two basic complexes, the Caribou and Memesagamesing intrusives, lie in the Canadian shield near the village of Loring. They are composed of norites with local picrites, pyroxenites and olivine norites. The feldspars vary in composition from An_{68} to An_{61} in the ultrabasics and olivine norites, and from about An_{63} to An_{48} in the norites. Orthopyroxenes vary from near En_{90} to En_{75} in the ultrabasics and olivine norites and from about En_{79} to En_{64} in the norites. The composition of the clinopyroxene in picrite is near $Wo_{38}En_{56}Fs_8$ and in pyroxenite near $Wo_{38}En_{52}Fs_{10}$. In the norites it varies from near $Wo_{39}En_{53}Fs_{10}$ to about $Wo_{41}En_{42}Fs_{37}$. The composition of the olivine is near Fo_{84} in picrite and near Fo_{83} in olivine norite. The picrite contains both ortho- and clinopyroxenes, but the early norite lacks the latter. As the orthopyroxene of the norite reaches a molar percentage of En_{76} augite appears and with continued crystallization it attains prominence.

A plot of the enstatite content of orthopyroxene against anorthite content of the plagioclase indicates a straight-line soda and iron enrichment relationship resulting from fractional crystallization and reflecting a temperature control. This linear relationship suggests

an approach towards equilibrium conditions. A plot of coexisting ortho- and clinopyroxenes indicates a linear increase of iron with progressive crystallization and suggests equilibrium conditions. In the (K_2O+Na_2O) - MgO - FeO diagram two trends distinguish themselves, magmatic and metasomatic. The former is one of iron enrichment and parallels the Mg - FeO side, The latter was caused by later granite pegmatites and parallels the calc-alkaline trend.

ISOTOPIC ANALYSIS APPLIED TO A CLIMATOLOGICAL PROBLEM

IRVING FRIEDMAN, DANIEL R. NORTON, A. C. REDFIELD AND D. B. CARTER

U. S. Geological Survey, Washington, D. C.

A study of the Lake Maracaibo, Venezuela, region was undertaken with the object of determining the water balance of the lake.

Hydrographic data indicate salinity in the lake is uniform and is about 1/25–1/30 that of sea water. The lake is well mixed and outflow data show that 1/10 to 1/15 of the lake flows out to the sea each year. $(22.0 \times 10^9 m^3)$ Inflow is about $0.7 \times 10^9 m^3/1$ year.

Using Thornthwaites' method, the upland runoff and rainfall of the lake were determined as $32.2 \times 10^9 m^3$ and $22.0 \times 10^9 m^3$ respectively. Deuterium determinations were made on the lake, river, and ocean waters. The deuterium balance requires that $33.5 \times 10^9 m^3/yr$ of water evaporate from the lake. This compares with $32.9 \times 10^9 m^3$ calculated from climatology data.

KUTNAHORITE: A MANGANESE DOLOMITE, $CaMn(CO_3)_2$

CLIFFORD FRONDEL AND L. H. BAUER

Harvard University, Cambridge, Massachusetts and New Jersey Zinc Company, Franklin, New Jersey

A re-examination of type material has shown that the kutnahorite of Bukovsky (1901) from Kutná Hora, Czechoslovakia, is a valid member of the dolomite group with the composition $Ca(Mn, Fe, Mg)(CO_3)_2$. The material of Žák (1949) from Chvaletice, Czechoslovakia, is shown to be similar. A third occurrence is described from Franklin, New Jersey: $CaCO_3$ 51.50, $MnCO_3$ 42.00, $MgCO_3$ 5.77, $FeCO_3$ 0.73 (mol per cent); n_D 1.728, n_E 1.535; a_0 4.85, c_0 16.34 Å; $S. G.$ 3.12. The DTA graph and x-ray powder pattern are very similar to those of ankerite, $CaFe(CO_3)_2$. Study of 46 specimens in the calcite-rhodochrosite series from Franklin, N. J., indicates that the series is incomplete under the particular genetic conditions at this locality, with a central gap extending from about 40 up to about 75 weight per cent $MnCO_3$.

A survey of the disordered calcite-type carbonates, olivine-type nesosilicates and NaCl-type oxides of Ca, Mn, Fe and Mg show that in the binary systems increasing similarity in ionic size is accompanied by increasing solid solution and decreasing tendency to form ordered phases. Further, in the binary series with a central gap, $(A,B)X - (B,A)X$, the smaller ion B substitutes to a larger extent for A in $(A,B)X$. An ordered dolomite-type phase $MnMg(CO_3)_2$ is predicted, and a possible example is cited. The ordered phase $FeMg(CO_3)_2$ is less likely, and three specimens found with essentially this composition proved to be of the disordered calcite-type, $(Fe,Mg)(CO)_3$.

INVESTIGATION OF DOMAINS IN REORDERED MINERALS

ALFRED J. FRUEH, JR.

University of Chicago, Chicago, Illinois

In many compounds that have ordered after existing in the disordered state, the basic structure is essentially a single crystal, while the super structure is divided into small do-

mains whose orientations, although bearing a rational relation to the more highly symmetric basic structure, are dissimilar.

In bornite (Cu_5FeS_4) where little or no change occurs in the dimensions of the basic structure during disordering, the domains are of less than 1000 Å in size as evidenced by diffuse super structure spots. In chalcopyrite (CuFeS_2) where a pronounced dimensional change occurs during disordering, the domains are larger.

The existence of anti-phase domains has been observed in natural occurring chalcopyrites in rocks where cubanite unmixing has occurred and in accessory chalcopyrite in metamorphic rocks of granulite facies.

THERMODYNAMIC RELATIONS AMONG THE URANIUM OXIDES, AND THEIR RELATION TO THE OXIDATION STATES OF THE URANIUM ORES OF THE COLORADO PLATEAUS

ROBERT M. GARRELS

U. S. Geological Survey, Washington, D. C.

Fields of stability of uranyl hydroxide and uranous hydroxide in water solution at 25° C. and one atmosphere pressure have been calculated as functions of Eh and pH. Equilibrium values of the activity of uranyl ion and of uranous ion also have been calculated and are shown as contours on the stability fields. Thermodynamic relations among the uranyl hydroxides, oxides, and hydrated oxides indicate that the free energy differences among the various species are small. The data are interpreted to mean that a variety of such uranium (VI) compounds may form and even co-exist. Similar studies of the uranium (IV) hydroxide indicates that it is unstable relative to the oxide and might well be expected to invert to the oxide at a finite rate. Uranium (V) compounds probably have a transitory existence because of the instability of the UO_2^+ ion; uranium (III) oxides and hydroxides would not be expected to occur naturally because the uranium (III) ion would decompose water. A comparison of the behavior of the low-valence vanadium hydroxides (III and IV) with uranium (IV) and (VI) hydroxides indicates that vanadium (III) hydroxide should oxidize to the vanadium (IV) hydroxide at a slightly lower potential than that required for the uranous to uranyl hydroxide pair. A speculative diagram showing probable fields of stability of many of the major minerals of the Colorado Plateaus is presented and the suggestion made that a consistent picture results if one assumes that the ores represent the superimposition of a weathering environment on a mineral assemblage formed in a primary reducing environment.

ABUNDANCE OF Sr^{87} DURING GEOLOGIC TIME

PAUL W. GAST

Dept. of Terrestrial Magnetism, Carnegie Institution, Washington, D. C., and
Lamont Geological Observatory, (Columbia University), Palisades, New York

The isotopic composition of "common" strontium from limestones and marbles of different ages has been determined. Samples include early Precambrian South African marble, middle Precambrian Grenville marble, Ordovician and Devonian limestones, and modern sea water. The change in the abundance of Sr^{87} relative to the stable Sr^{86} isotope is less than one-third of that expected (4.5% per billion years) from (a) the presently accepted abundances of Rb and Sr (Rankama and Sahama, 1951) in the upper crust, (b) the decay constant of Rb^{87} , and, (c) the assumption that the isotopic composition of strontium in the ocean is the same as the average isotopic composition of the strontium in the crust at any given time.

From this anomaly it is clear that one or more of the above assumptions is incorrect. A

critical examination of the geochemical cycle of radiogenic strontium, suggests that the mixing of radiogenic and common strontium is not complete during weathering and transport to the ocean. Such an effect is in the right direction to explain the anomaly. Another possibility is that the abundance of strontium relative to rubidium is greater than the value generally accepted in the literature.

GEOLOGY OF THE ENGER TOWER AREA, DULUTH, MINNESOTA

S. S. GOLDICH, R. B. TAYLOR, AND F. J. LUCIA

University of Minnesota, Minneapolis, Minnesota

In connection with studies of the Duluth gabbro that are being conducted by the Minnesota Geological Survey, the Enger Tower area in the City of Duluth has been mapped in detail. This area is considered to be representative of the upper part of the gabbro exposed in the Duluth region.

At least three periods of basaltic magma intrusion are recorded in the Enger Tower area. Anorthositic gabbro, the principal rock type, was derived in an early period. A second period of intrusion produced a zone of mixed rock types—quartz gabbro, granodiorite, and adamellite. A still later period resulted in basalt dikes.

Mesocratic uraltite gabbro is a roof phase of the anorthositic gabbro contaminated with fragments of basalt flows. Inclusions of anorthosite of the Beaver Bay type may represent an older period of differentiation.

Younger rocks that intrude the anorthositic gabbro are small bodies of granodiorite and hedenbergite granophyre and dikes of granite. These rocks constitute a series the origin of which is attributed to differentiation by fractional crystallization of basaltic magma. The line of descent is gabbro→granodiorite→calcic-granophyre→granite.

The effects of assimilation and of contamination are considered to be quantitatively unimportant in producing this rock series. Inclusions have been altered to hornfels, and marginal to the main granodiorite-granophyre intrusion, quartz and alkali-feldspar were introduced in the anorthositic gabbro.

Na CONTENT OF MICROCLINE

JULIAN R. GOLDSMITH AND FRITZ LAVES

University of Chicago, Chicago, Illinois

The amount of $\text{NaAlSi}_3\text{O}_8$ in solid solution in microcline (triclinic KAlSi_3O_8) can be determined by x-ray techniques. The a -axis spacing of microcline is the most sensitive to variation in the Na-content, analogous to the relation in monoclinic KAlSi_3O_8 . It is convenient to measure the (400) spacing by comparison with a simultaneously irradiated standard. The standard used here is a single phase, highly triclinic authigenic microcline, containing not more than 1% $\text{NaAlSi}_3\text{O}_8$. Microcline has not been synthesized, so the authigenic material is invaluable for establishing the lattice constants of the pure triclinic end-member.

If one assumes that the effect of Na on the a -axis of microcline is the same as its effect on sanidine, the data of Donnay and Donnay for the high temperature series can be used to construct a curve between microcline and albite. The validity of this assumption has been checked by plotting a -axis values of authigenic microclines with known quantities of Na introduced. Inasmuch as the a -axis of triclinic KAlSi_3O_8 differs slightly from that of monoclinic KAlSi_3O_8 , a correction for trilinearity must be made. The correction for "fully triclinic" microcline is approximately 9% for pure KAlSi_3O_8 , and varies with Na-content. Correction for microclines with intermediate trilinearity is also easily made.

Sizeable amounts of Rb in some microclines can lead to erroneous values. The data on

hand indicate that most microclines have exsolved virtually all of their albite; the common microclines appear to have 5% or less $\text{NaAlSi}_3\text{O}_8$ in solid solution.

DETAILED STRUCTURE OF NEPHELINE

THEODOR HAHN AND M. J. BUERGER

Massachusetts Institute of Technology, Cambridge, Massachusetts

The detailed refinement has been made of the nepheline structure. This has been based on new single-crystal Geiger counter measurements of $F^2(hk \cdot 0)$ and $F^2(hh \cdot 1)$. With these new data, two successive electron density projections $\rho(xy)$ and $\rho(xz)$, and difference syntheses, $\Delta\rho(xy)$ and $\Delta\rho(xz)$ were made. The second difference syntheses displayed an appreciable improvement in the relief, and corresponded to an improvement of the R factor. Because of overlapping in some of the atoms, no further improvement could be attained by refinement of projections. Accordingly, strategically located sections were prepared through the 3-dimensional electron density function. These syntheses made use of all new Geiger counter intensities plus additional upper-level intensities from the earlier photographic determination. The sections were synthesized on *X-RAC* with the kind permission of Professor Ray Pepinsky.

With these sections, the x , y , and z parameters of all atoms could be determined and some interesting and unsuspected features of the nepheline structure were revealed: The oxygen atom, ideally on the 3-fold positions, is off the axis and statistically occupies at least two nearby sets of 3-fold positions. The sodium atom too is distributed between two positions. Another oxygen atom in the general position also appears to occupy statistically two different locations. All other atoms are substantially fixed since sections through the electron density function show these atoms to be essentially spherical.

STUDIES IN THE SYSTEM CaO-MgO-CO_2

R. I. HARKER AND O. F. TUTTLE

The Pennsylvania State University, State College, Pennsylvania

Apparatus has been constructed to generate and apply a high pressure (100,000 psi) of CO_2 to cold-seal quenching units.

The p - T curve for the dissociation of dolomite, represented by the equation $(\text{CaMg}(\text{CO}_3)_2 = \text{CaCO}_3 + \text{MgO} + \text{CO}_2)$, passes through the points at 940°C. and 40,000 psi, 900°C. and 30,000 psi, 850°C. and 20,000 psi and at 800°C. and 10,000 psi. The corresponding curve for magnesite ($\text{MgCO}_3 = \text{MgO} + \text{CO}_2$) follows very nearly parallel to the dolomite curve between 40,000 and 10,000 psi but at about 50°C. below it. Some runs have been made to locate the calcite curve ($\text{CaCO}_3 = \text{CaO} + \text{CO}_2$) which is thought to be at somewhat lower temperatures than those previously determined by Smyth and Adams.

The sub-solidus relations in the system $\text{CaCO}_3\text{--MgCO}_3$ have been examined between 500 and 900°C. and it is found that solid solutions containing up to 51 per cent dolomite in calcite are stable at 900°C. and at pressures sufficiently high to prevent the dissociation of dolomite. Metastable solid solutions between calcite and dolomite have been synthesized and found to contain 64, 77 and 86 per cent of the dolomite component suggesting that complete solid solution may be found to be stable at higher temperatures. There is evidence of slight solid solution of calcite in dolomite and of dolomite in magnesite but the amount of magnesite in solid solution in dolomite was found to be negligible in the 500 to 900°C. range.

ISOTOPIC COMPOSITION OF Sr IN THE HOMESTEAD METEORITE

L. F. HERZOG AND W. H. PINSON, JR.

Massachusetts Institute of Technology, Cambridge, Massachusetts

The Homestead meteorite is a typical chondrite, containing 11% metal phase. Sr and Rb contents, determined by optical spectrographic analysis are: $Sr = 0.0020 \pm 0.0006\%$; $Rb = 0.0013 \pm 0.0004\%$, indicating precision of analysis only. The relative abundances of the Sr isotopes have been determined with a solid-source mass spectrometer and are the averages of 148 individual magnet-sweep, single collector determinations. The relative abundances are: $87/86 = 0.740 \pm 0.003$; $87/88 = 0.0881 \pm 0.0003$; $86/88 = 0.1192 \pm 0.0002$; $84/88 = 0.0058 \pm 0.0008$. A single double-collector measurement agrees with these measurements. The 86/88 ratio is identical with that of standard terrestrial Sr, while the 87/88 ratio is 5% greater.

Calculation of the age requires knowledge of the initial ^{87}Sr relative abundance. If this abundance was no greater than 0.0690 (the lowest value found in terrestrial rocks or minerals by our analyses) the minimum age would be 1 to 3×10^9 years, within the limits of uncertainty in the Sr and Rb measurements stated above. Other reasonable assumptions yield greater ages.

Analysis of a second meteorite (Pasamonte), with a considerably higher Sr/Rb ratio is in progress, and may provide knowledge of the initial ^{87}Sr abundance. The Sr/Rb ratio will be determined by isotope dilution analysis.

AGE DETERMINATIONS ON ZIRCON BASED ON RADIATION-DAMAGE MEASUREMENTS

HEINRICH D. HOLLAND, WILLIAM B. HEAD, III, AND GEORGE G. WITTER, JR.

Princeton University, Princeton, New Jersey

Age determinations based on measurements of the ratio of radiation damage to present alpha activity have been carried out on zircons from northern New Jersey, North Carolina, Southern Ontario, and the Adirondacks. The increase in the c -dimension of the unit cell of zircon has been used as a measure of radiation damage. The results are in good agreement with other age measurements on material of probably equivalent age and with ages found for the same materials by the lead-alpha activity method. It is concluded that radiation damage measurements in zircon can serve as the basis for a reliable method of age determination, and that the method will be particularly useful for homogeneous zircons which have received a radiation dosage between 50×10^{13} and 300×10^{13} alpha disintegrations per mg.

RELATIONS OF REGIONAL AND THERMAL METAMORPHISM NEAR THE BASE OF THE STILLWATER COMPLEX, MONTANA

ARTHUR L. HOWLAND

Northwestern University, Evanston, Illinois

Precambrian granite and metamorphosed sedimentary rocks form the main core of the Beartooth Mountains in south-central Montana. A study of the relationship of these rocks to the Stillwater igneous complex along the northern border of the range has been made by the U. S. Geological Survey. In the western part of the Stillwater complex the metamorphosed sedimentary rocks, consisting largely of a pelitic series, but containing some quartzite and iron-formation, are adjacent to the base of the complex and extend several miles southward from it. To the east, granite is in contact with the base of the complex except where small patches of sedimentary rocks are preserved at the base or as masses within the granite. Thermal metamorphism by the complex precedes the regional meta-

morphism and the emplacement of the granite as shown by the following: (1) Close to the base of the Stillwater complex high-temperature thermal metamorphism, associated with the intrusion of the complex, has altered the pelitic rocks, presumably originally of low-grade regional metamorphic facies, to cordierite-hypersthene-biotite-quartz hornfels and the iron-formation to quartz-magnetite-fayalite-pyroxene hornfels. (2) Away from the influence of the complex the sedimentary rocks are regionally metamorphosed to garnet-quartz-mica schist and partly granitized. (3) The granite, where it lies near the thermally metamorphosed zone, has partly converted hornfels to schist. The alteration of cordierite to sericite is the first sign of nearness of the granite.

ROLE OF WATER IN METAMORPHISM OF ROCKS IN THE CUCAMONGA CANYON AREA, CALIFORNIA

K. JINGHWA HSU

University of California, Los Angeles, California

The rocks of the Cucamonga Canyon area, California, have been subjected to two periods of metamorphism. Metamorphic rocks of the granulite facies were converted to amphibolites and mylonites in belts of intense fracturing during a post-granulite metamorphism. Mineral assemblages of the granulite facies in belts that were little deformed, however, were not altered to minerals of the amphibolite facies.

As the temperature and confining pressure during the second period of metamorphism were probably uniform over the small area about Cucamonga Canyon, the intimate association of granulite and amphibolite facies minerals suggests that local differences in vapor pressure of H_2O may have played an important role in determining the equilibrium assemblage. Thus Eskola's concept of metamorphic facies should be modified as the equilibrium assemblage of a rock of given bulk composition depends not only upon temperature and hydrostatic pressure, but also upon vapour pressure of H_2O in equilibrium with anhydrous and hydrated minerals (P_{H_2O}), and possibly upon some other factors. This conclusion can be reached independently from thermodynamic considerations.

Water was introduced during the second period of metamorphism preferentially into the pyroxene-rich rocks, probably because P_{H_2O} is lower for such rocks than for felsic rocks which are interbedded. Consequently, active syntectonic neomineralization (involving hydration of granulite minerals) was possible in mafic rocks, forming granoblastic amphibolites, while the felsic rocks underwent cataclastic deformation, forming mylonites.

MAGMATIC TRENDS AND AGE DETERMINATIONS OF PRECAMBRIAN INTRUSIVES OF CENTRAL TEXAS

R. M. HUTCHINSON,¹ H. W. JAFFE² AND DAVID GOTTFRIED²

¹Kansas State College, Manhattan, Kansas, and ²U. S.

Geological Survey, Washington, D. C.

Harker variation diagrams have been plotted for 17 intrusions: 8 Town Mountain type with 1 associated aplite; 1 Oatman type; 2 Sixmile type; 5 aplogranites, and 1 granite porphyry (llanite).

Town Mountain type granites occupy positions of lower and intermediate silica content. Aplogranites are restricted to high-silica positions. The aplite falls within the aplogranite range suggesting the aplogranites may be late stage differentiates of Town Mountain type granites. Llanite falls within the more acid of the Town Mountain type granites and probably is the approximate aphanitic equivalent.

Oatman type granite is intermediate between aplogranites and Town Mountain granites. Sixmile type granites fail to fit the curves suggesting a separate line of magmatic descent.

Age determinations are as follows:

Town Mountain type intrusions:	Wolf Mountain phacolith	917 million years
	Legion Creek mass	893 million years (av.)
	Enchanted Rock pluton	815 million years (av.)
Sixmile type:	Sixmile mass	822 million years
Oatman type:	Sharp Mountain mass	857 million years (av.)

Zircon samples from Wolf Mountain phacolith and Legion Creek mass gave low alpha counts compared with those from Enchanted Rock pluton and suggest a different period of intrusion or possibly fractionation with the uranium and thorium having concentrated in the younger fraction. High alpha counts of zircon from Sixmile mass and Sharp Mountain mass also indicate possible fractionation. The Town Mountain type granites probably had a common magma source, with different periods of intrusion.

Field relations confirm the age determinations. Sixmile mass crosscuts and contains xenoliths of Wolf Mountain phacolith. Enchanted Rock pluton contains xenoliths of schist recrystallized by intrusion of the Legion Creek mass.

PRELIMINARY REPORT ON INVESTIGATIONS OF MINERALS OF COLUMBIUM AND TANTALUM AND OF CERTAIN ASSOCIATED MINERALS

RICHARD W. HUTCHINSON

Newcastle, New Brunswick, Canada

The rotation properties of the columbite-tantalite series have been determined in detail and the results and their application to identification are discussed in the report on the investigation. The optical properties of some other columbium-tantalum minerals in reflected light, including yttrotantalite, bismutotantalite, stibiotantalite, tapiolite and ilmenorutile, have been determined. The relationship between the orthorhombic columbite-tantalite series and the tetragonal mossite-tapiolite series is critically examined. It is suggested that there is, in nature, only a single series with composition $(\text{Fe}, \text{Mn})\text{Cb}_2\text{O}_6$ - $(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$ and that this series includes the minerals columbite, tantalite and tapiolite with a change from orthorhombic to tetragonal symmetry in the tantalum-rich range. A disordered variety of the mineral tapiolite has been recognized and has a crystal structure of the rutile type. All specimens of ilmenorutile so far studied were found to be intergrowths of two minerals, columbite and rutile.

TEXTURAL RELATIONS OF CRYSTAL ACCUMULATES IN THE ULTRAMAFIC ZONE OF THE STILLWATER COMPLEX, MONTANA

EVERETT D. JACKSON

U. S. Geological Survey, Menlo Park, California

The igneous Stillwater complex is a differentiated layered intrusion at least 18,000 feet thick exposed for 30 miles along the front of the Beartooth Mountains, Montana. The lower 3,500 feet of the complex is composed of rhythmically stratified ultramafic rocks that exhibit both igneous and sedimentary textures. Mineral grains in the rocks can be divided into two types: individual euhedral crystals and negative-shaped grains interstitial to these crystals. Variations in size, shape, and composition of the well-formed grains are related to, and in many instances define, the layering. The interstitial material occurs in single grains or oikocrysts that are independent of the layering. The euhedral grains crystallized from the main magma and settled to the floor of the magma chamber; the interstitial grains crystallized in place from magma surrounding the settled crystals. The composition of the settled minerals is peridotitic: only olivine, orthopyroxene, and chromite occur as

euhedral individuals. The composition of the interstitial material is gabbroic: plagioclase, orthopyroxene, and clinopyroxene are the principal minerals. Where settled crystals were "cemented" by interstitial material belonging to a different reaction series, the original porosity of the crystal mush can be determined to have ranged from 20 to 40 per cent. Where settled crystals were secondarily enlarged or resorbed after accumulation by interstitial material belonging to the same reaction series, the rocks developed xenomorphic and hypautomorphic textures.

IGNIMBRITES IN SOUTHERN PERU

W. F. JENKS AND S. S. GOLDICH

University of Rochester, Rochester, New York and University
of Minnesota, Minneapolis, Minnesota

Ignimbrites near Arequipa were described in 1948 by Fenner and by Jenks. The ignimbrite (sillar) outcrops in 12% of the Arequipa quadrangle. It also occurs extensively in the Departments of Moquegua, Puno, Cusco, and Abancay, southern Peru.

Many tuff flows are related to an early phase of the present stream pattern. Single flows have been traced down valleys for 30 km.: in the headwaters they occupy valley bottoms; in the lower reaches valleys have been incised as much as 700 m. below the base of the tuff flows, leaving the flows on remnants of a mature surface. Thus these eruptions are related to the Chacra mature valley erosional stage, and were the last events before the rejuvenation which produced the present deep canyons.

Whereas the bulk of the Tertiary to Recent volcanics is andesitic, the sillar is rhyolitic. The sillar appears to have been a near-terminal phase of a long history of andesitic eruptive activity. The sillar in turn is locally covered by dominantly andesitic rocks of the latest cycle of vulcanism.

The sillar was erupted from diverse, dominantly andesitic volcanic massifs, but specific vents have not been found.

Ignimbrites of the Arequipa region are not welded. The hardness of those which are largely devitrified was attained by crystallization and cementation while the tuff flows were still hot, with the production of textures like those of previously described ignimbrites. Initial toughness of the ignimbrites is attested by their permanent displacement of major streams.

CORRELATION OF BASALT FLOWS IN CENTRAL NEW MEXICO BY FUSION TECHNIQUE*

HENRY L. JICHA, JR.

New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico

Late Tertiary and Quaternary basalt flows of at least five different ages from seven vents lie upon various surfaces in the Cerro Verde quadrangle, 50 miles northwest of Socorro New Mexico. The flows consist of olivine, augite, labradorite, magnetite, and glass and average about 48 per cent silica.

Powdered samples were fused in a carbon arc according to the method of Matthews, and refractive indices of glasses thus formed were determined to 0.001. Indices of 50 samples determined in the study range from 1.608 to 1.583. Duplicate fusions show that indices are reproducible to 0.002.

* Published by permission of the Director, New Mexico Bureau of Mines and Mineral Resources.

It was found that each flow has a specific range of refractive index not exceeding 0.015. Where these ranges do not overlap markedly, isolated flow remnants can be correlated on the basis of five or less samples. Vent rocks may also be correlated with flows derived from them.

The indices for three superposed flows from one vent are significantly different; each succeeding flow is more silicic. Statistical analysis shows that the probability of obtaining such variations from one population is less than 0.004.

The rapid fusion technique furnishes adequate basis for local correlation of basalt flow remnants as well as for correlation with filled vents. In all these samples compositional differences do not appear to be large enough to be revealed significantly by chemical analysis.

VARIATION IN THE ISOTOPIC COMPOSITION OF COMMON LEAD

J. LAURENCE KULP AND GEORGE L. BATE

Lamont Geological Observatory (Columbia University), Palisades, New York

New measurements of the isotopic composition of lead from some 120 lead minerals are reported. Some of these samples have been measured in several laboratories using Pb^{+} from PbI_2 , Pb^{+} from $Pb(CH_3)_4$, and $Pb(CH_3)_3^{+}$. In general the agreement is excellent indicating the absence of appreciable systematic error in any of the techniques.

This large increase in the data on common lead makes it possible to begin to predict the range in isotopic composition of lead from various geological settings. This is important for age determination and for the understanding of the mechanism of emplacement of lead ores. In the Joplin District the range in 207/206 is at least 4%, in the Wisconsin-Illinois-Iowa District at least 9%, and in S. E. Missouri 15%, although samples from opposite ends of a single crystal of galena showed no differences. The precision of measurement is 0.1 to 0.2%. These data strongly suggest that these leads were not derived from the mantle.

Variations in the isotopic composition of common lead from pegmatites in well-defined geological provinces such as New England or the Southern Appalachians appear much smaller. A few interesting exceptions to the regional pattern appear. One such exception occurs at Franklin, New Jersey.

The rough correlation of the isotopic composition with age persists. The new data do not greatly affect the calculation of the age of the earth, but do help delimit the area of application of the "galena age method."

VERTICAL CHANGES IN CHEMICAL COMPOSITION OF A PARTIALLY WEATHERED ILLINOIAN TILL

R. K. LEININGER, HAYDN H. MURRAY, AND HENRICH NEUMANN

Indiana Geological Survey, Indiana University, Bloomington,
Indiana, and Mineralogisk-Geologisk Museum, Oslo, Norway

The high wall of an abandoned strip coal mine in Clay County, Indiana, has provided a section including 40 feet of Illinoian till. Sixty-five channel samples were obtained; each sample represented 6 inches of section. Tests with dilute HCl and color differences indicated three distinct zones: (a) lower—unleached and unoxidized; (b) middle—unleached and oxidized; (c) upper—leached and oxidized.

This paper deals with the results of chemical and spectrographic analyses of the minus 200 mesh material and of water solutions obtained with the fine fraction of each sample. A concurrent investigation of the vertical changes in mineral composition is the subject of another paper.

Preliminary qualitative analyses proved unsatisfactory in the study because of the apparent similarity of the samples. Quantitative data for pH, Li, Na, K, Rb, Be, Mg, Ca,

Sr, Ba, B, Al, Y, Ti, Zr, V, Cr, Mn, Fe, Ni, Cu, Ga, C, Si, Pb, P, S, and F have shown some remarkable ranges of composition. For example, sulfur in the minus 200 mesh material increases from 0.3 per cent (as S) at the base to 0.6 per cent and decreases to 0.2 per cent in zone (a); it decreases further through zone (b) to a minimum of 0.005 per cent at the boundary of zones (d) and (c).

SANIDINE- AND ORTHOCLASE PERTHITES

W. S. MACKENZIE AND J. V. SMITH

Geophysical Laboratory, Washington, D. C.

A new rapid *x*-ray method for determining accurately the reciprocal lattice angles α^* and γ^* of the soda phase of perthites has been developed. Using this method the lamellar structure of a number of sanidine- and orthoclase perthites has been investigated in detail. Measurements of the reciprocal lattice angles α^* and γ^* of the soda phase give results which indicate that the composition of this phase may be determined from these angles.

The orthoclase micropertthites generally have a monoclinic potash phase and a soda phase corresponding to low-temperature albite or oligoclase. Specimens which have in addition a triclinic potash phase are found and these have values of optic axial angle greater than would be expected from their bulk chemical composition.

Sanidine cryptopertthites have a monoclinic potash phase and a soda phase which is not pure high-temperature albite but has a considerable amount of orthoclase in solid solution.

No perthites have been found having a soda phase which gives evidence of states transitional between high- and low-temperature soda feldspar although such forms have been postulated by other workers for single phase soda feldspar from both optical and *x*-ray studies.

DEVITRIFICATION IN PERLITE

ROYAL R. MARSHALL

California Institute of Technology, Pasadena, California

Perlites from many localities scattered throughout the western United States have been studied in thin section. The microcrystalline phase of perlites may be divided into two parts. One phase, consisting of crystallites and microlites is characteristic of all hypohyaline rocks and apparently reflects the composition and cooling history of the magma. It may be considered primary. The other phase, which may be considered secondary, consists of devitrified films on both sides of the perlitic cracks which are commonly filled with a secondary mineral. The devitrification bordering the cracks typically is highly irregular in outline and diffusely birefringent. This phase appears to have developed in many cases after cooling of the perlite. Photomicrographs illustrate the greater abundance of this secondary phase in the older perlites among the specimens examined. Thus, in an Eocene perlite, the film of devitrificatoin is 7 microns thick; in a Pliocene perlite, less than 1 micron thick.

To explain the transformation of the metastable glass phase into crystalline material, a mechanism involving the diffusion of water is introduced. Calculations indicate that the upper limit for the diffusion constant of water into natural glass in the neighborhood of 25° C. is $10^{-8}\text{cm.}^2/\text{M yr.}$

Hydrothermal alteration causes considerable variation in the penetration of devitrification inward from the numerous internal interfaces. This process and the presumed distribution of water in the perlites are correlated to explain the greater water content of the older perlites.

CaO-V₂O₅-H₂O SYSTEM

RICHARD MARVIN

U. S. Geological Survey, Washington, D. C.

As an aid in determining environmental conditions of naturally occurring hydrous calcium vanadates, an investigation was made of the CaO-V₂O₅-H₂O system. The variables of the system, in the order of their importance, are pH, temperature, and concentration. pH values ranged from 0 to 12; temperature from 25 to 90° C.; and the V₂O₅:CaO ratio from 0.5 to 10. The stability areas of eight crystalline phases were delineated. These phases can be divided into two major groups: the colorless phases, which are stable above pH 6.5; and the colored phases, which are stable below 6.5. According to the phase diagram, the stable phase below pH 2.2 at 25° C. (pH 3.0 at 90° C.) is hydrous vanadium pentoxide. Between 2.2 and 6.5 two naturally occurring minerals, hewettite and pascoite, are stable.

The stability field of pascoite is large at ordinary temperatures but gradually diminishes as the temperature rises and disappears at about 70° C.; at the same time the stability field of hewettite increases at the expense of the pascoite field. In the pH range from 6.5 to 7.5 and at temperatures less than 40° C., rossite is the stable phase. At higher temperatures several unnamed phases appear. At pH 7.5 to 10.0 two hydrous pyrovanadates(?) occur. Their stability range is influenced both by pH and by the V₂O₅:CaO ratio. Above pH 10, Ca(OH)₂ rapidly precipitates, and calcite forms if the solution is exposed to the atmosphere. Those phases whose stability field is near pH 7 seem to be the most soluble.

RADIOACTIVITY OF SOME RECENT BOTTOM SAMPLES FROM
LAKE PONTCHARTRAIN, LOUISIANA

JOHN C. McCAMPBELL

Tulane University, New Orleans, Louisiana

An examination by means of a scintillation detector and a scaling circuit of some recent bottom samples taken from Lake Pontchartrain has been carried out under carefully controlled conditions. Considerable variation has been found in the disintegration rates. The data collected have been compared with both mechanical and chemical analyses of similar samples taken from the area and a correlation has been made. The areas of finer textures show the higher counts and the area of low organic content likewise have higher counts than the areas of higher organic matter. The detrimental factors due to background count have been removed by heavy shielding and by the determination of the residual background before and after sample counting. In order to insure accuracy with such low counting rates as exhibited here, a counting time of five hours has been utilized.

NEW MINERALS, REEDMERGNERITE (Na₂O·B₂O₃·6SiO₂) AND EITELITE (Na₂O·MgO·2CO₂)
ASSOCIATED WITH LEUCOSPHEINITE, SHORTITE, SEARLESITE, AND CROCIDOLITE
IN THE GREEN RIVER FORMATION, UTAH*

CHARLES MILTON, JOSEPH M. AXELROD, AND FRANK S. GRIMALDI

U. S. Geological Survey, Washington 25, D. C.

Cores and cuttings from the Green River formation in Utah contain two new minerals, reedmergnerite and eitelite, with leucospheinite, searlesite, crocidolite, and shortite, in dolomitic shale. Reedmergnerite (Na₂O·B₂O₃·6SiO₂) occurs in many wells in Duchesne and Uintah counties as crystals rarely more than a millimeter long, colorless, triclinic, space group *P1* or *P1* forms (100)(001)(102)(101) in one zone, and (010)(100) and (210)

* Publication authorized by the Director, U. S. Geological Survey.

another; habit stubby prismatic; $D=2.69$; indices of refraction: $\alpha=1.560$, $\beta=1.564$, and $\gamma=1.572$. The name honors Frank S. Reed and John L. Mergner, technicians of the Geological Survey, whose skill has served petrological science for more than 40 years. Reedmergnerite and $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$ are the only known ternary phases of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, and apparently both must form hydrothermally under relatively low temperature and pressure.

Searlesite ($\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) occurs sparingly with eitelite, etc., the fourth reported occurrence and the first in Utah; however, J. J. Fahey, who described this mineral from Wyoming in 1950, also noted its presence in cores from the Green River formation in Utah in 1952.

Eitelite ($\text{Na}_2\text{O} \cdot \text{MgO} \cdot 2\text{CO}_2$) has been found only in the Carter Oil Company Kermit Poulson No. 1 around 2850 feet, in crystals a few millimeters in diameter. Indices of refraction: $\epsilon=1.450$ and $\omega=1.605$; good basal cleavage; agrees with hexagonal symmetry reported by Eitel and Skaliks, who synthesized it in 1929. This is the second of the alkali-alkali earth carbonates synthesized by Eitel and Skaliks found in nature, the other being fairchildite, $\text{K}_2\text{O} \cdot \text{CaO} \cdot 2\text{CO}_2$.

Eitelite is named to honor Wilhelm Eitel, Director, Institute of Silicate Research, University of Toledo, Ohio.

IGNEOUS PETROLOGY OF PARAGUAY*

CHARLES MILTON AND EDWIN B. ECKEL

U. S. Geological Survey, Washington, D. C.

A collection of igneous rocks made by E. B. Eckel in southern and east-central Paraguay as representative of the principal rock types of the region has been studied. Eight new analyses are given of granite, aplite, rhyolite, and quartz porphyry, two of basalt, and two of alkalic rocks—nepheline syenite and shonkinite. Each analysis is supplemented by spectrographic determination of 19 minor and trace elements. A widespread series of granitic, rhyolitic, and porphyritic rocks has been variously ascribed to ages ranging from Precambrian to Tertiary; however, all of these rocks have a notably consistent petrographic character, chemical composition, and suite of trace elements, suggesting that all of these rocks may be co-magmatic and essentially contemporaneous. No evidence of a stratigraphic nature opposed to this suggestion is known to the writers. The presence of boulders of such rock in conglomerate of Permian age indicates Paleozoic or older age for these silicic rocks. Among basaltic rocks and diabase is one occurrence containing well-developed pseudobrookite. A heretofore unrecognized suite of alkalic rocks, ranges from nepheline syenite to shonkinite; the latter contains an unusual type of kataphorite, similar to an amphibole previously known only from Wyoming and Western Australia.

The silicic rocks are presumably the southern extension of the Brazilian basement complex; the basaltic rocks are part of the vast Parana basalt of Triassic-Jurassic age of southeastern Brazil and eastern Paraguay; the alkalic rocks represent a group of magmas of relatively local extent but sporadically widespread; they may be younger than Precambrian. But no closer age designation can be made now.

ZONED PLAGIOCLASE IN METAMORPHIC ROCKS

PETER MISCH

University of Washington, Seattle, Washington

Since metamorphic plagioclase is often stated to lack normal, and especially recurrent, zoning, and since the presence of such zoning in a granitic rock is widely accepted as proof

* Publication authorized by the Director, U. S. Geological Survey.

of an igneous origin, the plagioclase was examined in a large number of varied, non-granitic, and unquestionably metamorphic rocks from different areas. Zoning, though on the whole less common than in certain igneous rocks, was found to be widely present, with normal more frequent than reverse zoning. Recurrent zoning was also observed, for instance in mica schist and calc-silicate granulite. Zoning varies from highly gradational to rather sharp, and from anhedral to euhedral. A low metamorphic grade, as well as strong syncrystalline deformation, are unfavorable for zoning. Petrographic features suggest different causes of zoning. (1) Thermal control may produce normal, reverse, or recurrent zoning in rocks containing "anorthite substitutes" (epidote, zoisite, calcite plus mica, Ca-scapolite, etc.), the ability of the plagioclase to incorporate anorthite molecule changing with the temperature, and a supply of potential anorthite being available. (2) Slow, very small-scale diffusion of Ca from more into less calcareous bands in higher grade rocks may cause reverse zoning. (3) Introduction of Na may produce normal zoning. (4) Contrasted to these cases of growth-zoning, passive or secondary normal zoning may occur if plagioclase is partially replaced by (a) Ca-rich minerals (epidote, hornblende), or (b) K-feldspar; preservation of the original plagioclase lattice in the more sodic secondary rims indicates microscopic lattice diffusion. In other cases, the causes of zoning remain obscure.

ORIGIN OF CALCAREOUS OÖLITHS

P. H. MONAGHAN AND MELBA L. LYTLE

Humble Oil & Refining Co., Houston, Texas

Laboratory studies were undertaken to discover mechanisms which might explain the origin of calcareous oöoliths in nature.

Calcium carbonate was precipitated from sea water by evaporation, by addition of precipitating agents, and by the growth of sulfate-reducing bacteria.

The effect of the major ions in sea water on the form of the calcium carbonate precipitate was studied.

From these studies the following conclusions may be drawn:

(1) Calcareous oöoliths or spherulites can be chemically precipitated from sea water if the carbonate ion concentration at the time of precipitation is greater than 0.002 mol per liter. This is a higher concentration than is found in normal sea water.

(2) Calcareous oöoliths may also be formed through the growth of sulfate-reducing bacteria in sea waters.

(3) The presence of the magnesium ion in sea water causes calcium carbonate to precipitate as aragonite rather than calcite.

(4) The laboratory conditions necessary for the chemical precipitation of calcareous oöoliths might be reproduced by an environment in which fresh waters high in carbonate ion flow into a shallow sea. Such a mechanism does not appear to be responsible for any large present day deposits.

(5) Environments where sulfate-reducing bacteria might be important in the origin of calcareous oöoliths should be characterized by deficiency of oxygen, increased pH, and presence of hydrogen sulfide or sulfide salts. Such environments might be highly localized.

VERTICAL CHANGES IN MINERALOGICAL COMPOSITION OF A PARTIALLY WEATHERED ILLINOIAN TILL

HAYDN H. MURRAY, RICHARD K. LEININGER, AND HEINRICH NEUMANN

Indiana University, Indiana Geological Survey, Bloomington, Indiana, and
Mineralogisk-Geologisk Museum, Oslo, Norway

This study gives the vertical changes in mineral composition of a partially weathered Illinoian till section described in a paper by the same authors concerning the vertical

changes in chemical composition. The minerals were identified using the petrographic microscope, x-ray diffraction, and differential thermal analysis. The minerals in the minus 20 to plus 200 mesh range were examined in some twenty samples, but the major work was done on the minus 200 mesh fractions of sixty-five samples.

The minus 200 mesh fractions in the lower, unoxidized, unleached zone (assumed to be unaltered till) contain mostly quartz, calcite, dolomite, feldspar, kaolinite, illite, chlorite, and a small amount of montmorillonite. The same fractions in the middle, oxidized, unleached zone contain the same minerals; however, the crystallinity of the clay minerals, illite and chlorite, decreases, presumably because of oxidation of iron, and the amount of montmorillonite increases slightly. In the minus 200 mesh fractions of the upper, oxidized leached zone, primary calcite and dolomite disappear; kaolinite, illite, and chlorite either disappear or are present in very small amounts. The amount of montmorillonite increases markedly in the upper, highly weathered zone; this fact is contrary to expectations because kaolinite is usually considered to be the most stable clay mineral. Organic material is present in the unoxidized zone, but disappears almost completely in the oxidized zones.

THE STRUCTURAL SCHEME OF SEPIOLITE

BARTHOLOMEW NAGY AND W. F. BRADLEY

The Pennsylvania State University, State College, Pennsylvania
and Illinois State Geological Survey, Urbana, Illinois

An idealized structural scheme for sepiolite is deduced from the observed x-ray diffraction effects in the zero layer line of diagrams obtained from several natural fibres. The structure consists of a centered array of linked chains of composition $H_6Mg_3Si_{12}O_{30}(OH)_{10} + Aq$ somewhat similar to those found in attapulgite, the chains serving to enclose a second centered array of channels in which molecular water is disposed.

The $hk0$ projection is orthogonal with $a = 13.4\text{\AA}$ and $b = 27\text{\AA}$. The skeletal chains are centered about $0, 0, Z$ and $\frac{1}{2}, \frac{1}{2}, Z$. Mg sites for each chain are at $x=0$ and $y=0, \pm 1/18, \pm 2/18, \pm 3/18$, and $\pm 4/18$. Oxygen and hydroxyl, silicon, and oxygen, in layers, fill out each chain coordinated as in a mica or a chlorite, and the eight oxygens at $\frac{1}{2}, \frac{1}{2}, Z$ are each links common to two chains. The water channels are centered about $\frac{1}{2}, 0, Z$, and $0, \frac{1}{2}, Z$.

The disposition of the eight octahedral ions (mainly Mg) indicated by chemical analysis among the nine positions available in the schematic chain is not specified.

The quality of agreement between calculated and observed $hk0$ type intensities is illustrated. It is considered to adequately confirm the idealized section. It seems probable that the entire structure is in $C 2/m$.

MANGANESE CONTENT OF GARNETS FROM THE FRANCISCAN SCHISTS

A. PABST

University of California, Berkeley, California

Many years ago Pabst described "The garnets in the glaucophane schists of California" (*Am. Mineralogist*, 16: 327-333, 1931) reporting a very low manganese content. In summarizing, the range of the spessartite content was given as "0-1%."

Several years ago, at the suggestion of Dr. Max D. Crittenden, some of these garnets were reexamined. New determinations indicated that the 1931 report of manganese content was seriously in error.

Nearly two years ago, in response to an inquiry, the writer informed Dr. Schürmann of the Hague of this error and indicated the correction. In spite of this Dr. Schürmann (*Neues Jahrb. f. Min.*, 85: 303-394, 1953) has recently cited my old erroneous figures without comment.

Recently a full analysis of a garnet from eclogite associated with glaucophane schist near Healdsburg, California, has been reported by Dr. Iris Borg. This also shows a more than negligible amount of MnO.

Thanks to the courtesy of Drs. Borg and Crittenden it is now possible to make the corrected statement in the following table:

Garnet	MnO	S. G.	N _{Na}	a_0
	wt.			
Hilton Gulch, Santa Clara Co., Calif., "A" of Pabst, 1931.	2.03%	3.95 ± 0.04	1.795 ± 0.002	$11.62 \pm 0.01 \text{ \AA}$
South of Calaveras Valley, Santa Clara Co., Calif., Crittenden, 1951.	4.63	4.00 ± 0.05	1.795 ± 0.002	11.61 ± 0.01
Near Junction School, Healdsburg Quad., Calif., Borg, 1954.	0.92	4.08 ± 0.02	1.795 ± 0.003	11.62 ± 0.01

The last column of table III in Pabst (1931) should be revised to read "range of grossularite 8–30%, andradite 4–24%, almandite 48–56%, pyrope 16–20%, spessartite 1–10%." The order remains as before even though the spessartite limit is raised by a factor of 10.

PETROLOGY OF SPODUMENE-BEARING PEGMATITES

LINCOLN R. PAGE

U. S. Geological Survey, Denver Federal Center, Denver, Colorado

The wide variety of petrologic types of spodumene-bearing pegmatities is the result of differences in the initial composition of magmas, mode of emplacement, crystallization history, and simultaneous deformation of the wall rocks. An individual body may have formed by cooling of single or multiple masses of magma, with or without metasomatic replacement. Each body is composed of at least two distinct mineralogic and structural units; some bodies are composed of as many as 13 units. Spodumene-perthite, spodumene-perthite-amblygonite-albite-quartz, spodumene-albite-quartz, and spodumene-quartz are the most common mineral assemblages in lithium-rich units. The long axes of spodumene crystals—either fresh or altered—may be oriented parallel or at right angles to the wall-rock contacts, at right angles to the zonal contacts, parallel to pre-existing gneissoid banding, or at random.

Spodumene is commonly the first mineral to form in the pegmatite unit and acts as a locus for crystallization of albite. The early-formed spodumene crystals may react completely with rest liquids to yield pseudomorphs composed of clay, mica, and other minerals; less complete reaction commonly results in corroded and rounded crystals.

Flow structures, broken crystals, and deformed wall rocks indicate forceful intrusion of initial viscous lithium-bearing magmas; other orientations of spodumene within the units are the result of crystallization during regional deformation or under static conditions. Replacement units rich in spodumene form as the result of abrupt changes in physical conditions during crystallization.

VARIATION DIAGRAMS ON TRIANGULAR COORDINATES OF ORTHOMAGMATIC AND METASOMATIC SUITES

FORBES ROBERTSON AND G. E. GOODSPEED

University of Washington, Seattle, Washington

Suites of chemical analyses of orthomagmatic rocks exhibit distinctive symmetrical patterns which are considered to represent different modes of magmatic differentiation. Metasomatic granitic rock suites, on the other hand, show erratic patterns. Mobilized feldspathized rocks show a tendency towards symmetrical patterns.

The diagrams are a modification of Larsen's triangular diagrams. Norms are computed from chemical analyses after the C.I.P.W. system and adjusted to 100 per cent. Feldspars, mafics, and quartz are plotted. (Silica deficiency is plotted below the zero quartz line.) The Or-Ab-An ratios are superimposed respectively. Lines connect the two points obtained from a single analysis and serve to emphasize the symmetrical or erratic characteristics of the diagrams.

Orthomagmatic suites include: volcanic rocks from several localities; rocks from layered intrusions; and rocks from igneous granitic bodies of batholithic dimensions.

Metasomatic suites include rocks from localities where the interpretation of granitization has been advanced and also from localities where the field and petrographic evidence suggests granitization.

VERTICAL DIFFERENTIATION IN THE WHITE TANK QUARTZ MONZONITE

JOHN J. W. ROGERS

224 S. Linden Drive, Beverly Hills, California

The White Tank quartz monzonite, of possible Jurassic age, forms four distinct plutons in Joshua Tree National Monument just south of Twentynine Palms, Calif. The largest of these plutons (seven miles in diameter), shows a variation of composition and texture through a vertical range of 1000 feet from the actual roof to the lowest exposed rock (probably not the true base).

The principal upward changes in the pluton are: potash feldspar increases from 20% to 50%; grain size of potash feldspar changes from three to eight millimeters, and color changes from pink to gray; biotite decreases from 10% to 3%; composition of the principal plagioclase changes from $Ab_{70}An_{30}$ to $Ab_{85}An_{15}$; the amount of myrmekite and "vein" perthite increases. The ratio between the amounts of quartz and plagioclase is roughly the same throughout the pluton, and the sizes of quartz and plagioclase are constant. The upper part of the pluton contains irregular intergrowths between microcline and sodic oligoclase, distinct albitic borders on some plagioclase laths where they contact potash feldspar, and rare graphic texture. The myrmekite is largely restricted to the albitic rims.

It is believed that the compositional and textural variations may be explained by simple crystallization differentiation of an intruded melt and enrichment of the later fluids in water. All of the observed textural features may logically form by primary crystallization.

GOLDICHITE, A NEW HYDROUS POTASSIUM FERRIC SULFATE FROM THE SAN RAFAEL SWELL, UTAH

A. ROSENZWEIG AND EUGENE B. GROSS

University of Minnesota, Minneapolis, Minnesota and U. S. Atomic Energy Commission, Grand Junction, Colorado

Goldichite, a new hydrous potassium ferric sulfate from the Dexter No. 7 Mine, Calif Mesa, San Rafael Swell, Utah, has the composition $KFe(SO_4)_2 \cdot 4H_2O$. It occurs as radiating

clusters of pale-green crystals or fine-grained crystalline encrustations. It is associated with coquimbite, halotrichite, roemerite, alunogen, copiapite, fibroferrite, melanterite and other sulfates, which comprise the cementing material of a talus slope below a small, pyrite-rich uranium deposit in the Triassic Shinarump conglomerate. Crystals are commonly singly terminated, monoclinic-prismatic laths parallel {100} with forms {100}, {110}, and {011}. The space group is $P2_1/c$ and the cell constants are: $a_0 = 10.45 \text{ \AA}$, $b_0 = 10.55 \text{ \AA}$, $c_0 = 9.15 \text{ \AA}$, $\beta = 101^\circ 49'$. The cell contains 4 molecules; the density is 2.43 (observed) and 2.419 (calculated). The mineral is biaxial positive, with $2V = 82^\circ$ (calculated), $\alpha = 1.582$, $\beta = 1.602$, $\gamma = 1.629$; $X = b$, $Z/\epsilon = 11^\circ$.

The mineral is named in honor of Samuel S. Goldich, Professor of Geology at the University of Minnesota.

LAYERED BASIC INTRUSIVE, FAIRWEATHER RANGE, SOUTHEASTERN ALASKA

DARWIN L. ROSSMAN

U. S. Geological Survey, Menlo Park, California

In 1952 the U. S. Geological Survey examined one of three known layered basic intrusive bodies in the Fairweather Range, southeastern Alaska. The body is roughly elliptical in plan, about 16 miles long and 8 miles wide. It is distinctly layered. The layers form a bowl-shaped structure similar to that of the Skaergaard complex, but this body differs in that the contacts are essentially vertical. About 32,000 feet of layered rock is exposed, but neither the top nor the bottom is visible. The structure, metamorphism of enclosing rocks, and contact relations suggest that the body is intrusive.

The rock-forming minerals, plagioclase and clino- and ortho-pyroxene, do not show significant change in composition throughout the entire sequence. The ratio of light to dark minerals within a layer or groups of layers suggests that the layers are genetically related and were formed by the same precisely repeated mechanism. A plot of the specific gravities of about 600 rock specimens fails to show any recognizable trend within the exposed portion. The relation of observed structures within layers to the genesis of the body is discussed.

SYNTHETIC ALKALINE EARTH GERMANATES ISOSTRUCTURAL WITH ENSTATITE AND PSEUDOWOLLASTONITE

ROBERT S. ROTH

National Bureau of Standards, Washington, D. C.

Germanium dioxide, of the α -quartz structure, when heated with equi-molar per cents of MgO, CaO, SrO, and BaO, at $1,235^\circ \text{C}$. for one hour, was found to form ABO_3 -type compounds. The MgGeO_3 compound was found, by x -ray diffraction, to be isostructural with enstatite (MgSiO_3). This Ge-enstatite is orthorhombic with $a = 18.661 \text{ \AA}$, $b = 8.954 \text{ \AA}$ and $c = 5.346 \text{ \AA}$. SrGeO_3 and BaGeO_3 were found to have structures similar to pseudowollastonite (α - CaSiO_3). However the structure of CaGeO_3 was not definitely established to be of this form. X -ray patterns of the pseudowollastonite-type structures indicate that larger A and/or B ions tend to increase the symmetry of the structure. α - CaSiO_3 itself is only pseudohexagonal but BaGeO_3 appears to be truly hexagonal.

As GeO_2 is known to have a rutile-type polymorph, with Ge^{+4} ions in octahedral coordination, it was thought possible that these silicate-type structures might have titanate-type polymorphs. GeO_2 can be readily formed in the rutile-type structure by heating the quartz-type polymorph at 700°C . and 20,000 psi. However, the pseudowollastonite-type BaGeO_3 , when heated under 20,000 psi at 700°C . showed no change in crystal structure. Differential thermal analysis of BaGeO_3 indicates a phase transformation at about 340°C . A 1% addition of Fe_2O_3 to BaGeO_3 causes an entirely different x -ray pattern which may represent the stabilized form of high temperature BaGeO_3 .

RECONNAISSANCE OF THE SYSTEM $\text{Na}_2\text{O-FeO-SiO}_2$

J. F. SCHAIRER, H. S. YODER, AND A. G. KEENE

Geophysical Laboratory, Washington, D. C.

More than seventy separate compositions in this system have been prepared and studied by the method of quenching. The fields of fayalite, wüstite, tridymite, quartz, sodium metasilicate and sodium disilicate have been delineated. There are many new ternary compounds whose compositions, fields of stability, and mutual melting relations are very difficult to determine because of the change in composition of melts by reaction with the container, an iron crucible, and because of the crowding of the fields of many of these compounds into a very small portion of the phase diagram. A preliminary diagram for this system is presented at this time.

Phase data on this system and its analog $\text{Na}_2\text{O-MgO-SiO}_2$ are necessary before proceeding to studies of more complex systems which may help us to determine the relationships between alkaline pyroxenes and amphiboles which are important constituents of some of the alkaline rocks and minor mineral constituents of many igneous rocks.

VOLCANIC ROCKS OF SAIPAN, MARIANA ISLANDS*

ROBERT GEORGE SCHMIDT

U. S. Geological Survey, Washington, D. C.

The Mariana Islands are divisible into two separate chains—the Southern Marianas, which include Saipan, aligned along an eastern arc and consisting of Tertiary volcanic rocks and limestones; and the northern Marianas, forming a western arc of Quaternary volcanoes.

The volcanic rocks of Saipan consist of dacitic and andesitic flows and pyroclastic rock of Eocene and probable Oligocene age. The dacites are composed primarily of silicic glass, oligoclase, silica minerals, and magnetite. The andesites are composed principally of labradorite, hypersthene, augite, magnetite, silica minerals, and anorthoclase. Chemically, the rocks are characterized by a high content of silica and alumina and a low content of potash. Quartz is universally present in the norm, attaining as much as 49 per cent in the dacites. The andesites are extremely calcic and contain a large excess of lime over alkalis.

The andesites and dacites of Saipan generally bear a close compositional resemblance to volcanic rocks of other islands in the system of arcs extending from Japan to Palau. Apparently the bulk of the volcanic rocks in this region form a well-defined petrographic province.

It is difficult to reconcile the andesitic and dacitic rocks with simple differentiation of a primary basaltic magma. Providing they are related to ancestral basaltic rocks, it seems necessary to assume assimilation of important amounts of siliceous and aluminous crustal material to account for their composition. The absence of basalts on Saipan and the wide compositional gap between the andesites and dacites may indicate that the andesitic and dacitic magmas originated independently.

MINERALOGICAL MAGIC NUMBERS

CECIL J. SCHNEER

University of New Hampshire, Durham, N. H.

Axial ratios c/a in the proportions 2, 3, 4, 15, 6, 21, 8, . . . , recorded for one dimensional isomorphous series such as the rare earth carbonates and iron sulfate hydrates, and

* Publication authorized by the Director, U. S. Geological Survey.

for one dimensional polymorphs such as silicon carbide and zinc sulfide, can be explained by a superlattice principle of general applicability. Each of the axial ratio numbers represents the number of layers in the unit cell of a particular phase. The smaller layer numbers of the isomorphs occur at simple stoichiometric ratios of the end-member components. The smaller layer numbers of the polymorphs occur at simple stoichiometric ratios of the end-member structural arrangements. Choice of stoichiometric ratio is a function of temperature. Given a fixed stoichiometric ratio, summation of interaction potentials between layers shows that an orderly distribution of the two types of layers minimizes the potential. Superlattices result from ordering. The "magic numbers" remain, even with compositional departure from simple stoichiometric proportions, because of the higher entropy of the simple ratios. From this point of view, complete isomorphism or a continuous series is possible only with disequilibrium. At equilibrium, the stable phases form a discontinuous or discrete series.

CHEMICAL EVIDENCE OF POSSIBLE GRANITIZATION OF THE FORDHAM GNEISS, NEW YORK

DAVID M. SCOTTFORD

Miami University, Oxford, Ohio

Evidence of a possible granitization origin for the Poundridge granite, Westchester County, New York, is afforded by calculations of Barth's standard-rock cell. Since there is no evidence of any expansion in the migmatite, a comparison of the standard cells of the Fordham gneiss and the migmatite gives an accurate picture of the exchange of cations which produced the migmatite by metasomatism of the gneiss.

Cations added	Cations subtracted
4.3 Si	.1 Ti
2.8 K	1.5 Al
—	1.2 Fe ³⁺
7.1 Cations representing	2.0 Fe ²⁺
20 valences	1.0 Mg
	2.1 Ca
	.6 Na
	.6 H
	—
	9.1 Cations representing
	20 valences

A similar comparison of the migmatite and Poundridge granite indicates that the following exchange could have produced the granite.

Cations added	Cations subtracted
5.6 Si	.2 Ti
.1 Fe ³⁺	4.4 Al
1.1 K	.9 Fe ²⁺
—	1.3 Mg
6.8 Cations representing	1.3 Ca
23.4 valences	1.3 Na
	1.2 H
	—
	10.6 Cations representing
	23.5 valences

The very similar pattern of the two exchanges shows that the granite could well have been a product of the same metasomatic process which produced the migmatite. The difficulty in assuming the migmatite to be the result of the simple addition of silicon and potassium from a granite magma lies in accounting for the lost ions removed from the gneiss. There is nothing inconsistent in the composition of the Fordham gneiss to destroy the possibility that these ions were displaced outward into the surrounding gneiss. It is also possible that they became concentrated in the ubiquitous amphibolite layers which characterize the gneiss.

SYNTHESIS AND ATOMIC STRUCTURE OF LORENZENITE

ROBERT F. SHURTZ

The Research Laboratory in Ceramics, The University of Texas, Austin, Texas

Lorenzenite is the name of the naturally occurring compound $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$ in which ZrO_2 may substitute for TiO_2 to the extent of nearly 12% ZrO_2 by weight.

Synthesis of lorenzenite has been previously reported. This synthesis cannot be repeated and it is shown here that rutile was mistaken for lorenzenite in this early report. A successful and reproducible synthesis from systems containing fluorine is described in this paper. The indices of refraction and the x-ray diffraction pattern of the synthetic lorenzenite confirm the synthesis.

The space group of lorenzenite has been reported as $D_{2h}^{14}\text{-Pbcn}$ with a_0 —14.51 Å, b_0 —8.73 Å, and c_0 —5.22 Å. This space group has been redetermined and confirmed using Weissenberg photographs. However, the orientation is found to be a_0 —8.66 Å, b_0 —5.18 Å, and c_0 —14.42 Å. There are four molecules of composition $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$ in the unit cell.

The atomic coordination scheme of lorenzenite has been deduced with sufficient accuracy that refinement by the use of Fourier or Patterson series would be relatively easy should such refinement become desirable. The structure consists of chains of titanium octahedra, similar to those in brookite, in parallel coordination with chains of silicon tetrahedra, similar to those in the pyroxenes. The growth habits, physical properties and diffraction intensities are in accord with this preliminary structure for lorenzenite.

ISOTOPIC COMPOSITION OF CARBON IN PETROLEUMS AND OTHER ORGANIC CONSTITUENTS OF SEDIMENTS

S. R. SILVERMAN AND S. EPSTEIN

California Research Corporation, La Habra, California and
California Institute of Technology, Pasadena, California

$\text{C}^{13}/\text{C}^{12}$ ratios of petroleum and other organic sedimentary constituents vary by more than three per cent. C^{13} content of organic carbon occurring in nonmarine deposits is appreciably lower than that of organic carbon associated with marine sediments. This difference may be due to inherent differences in source materials because fresh water plants and land plants contain less C^{13} than do marine plants and animals.

Variations in carbon isotope abundances in petroleum are related also to petroleum composition. Paraffinic and naphthenic constituents separated in the laboratory from a California crude oil are low in C^{13} content, whereas aromatic constituents are enriched in C^{13} relative to the C^{13} content of the total crude oil.

FORM AND MODE OF EMPLACEMENT OF SILLS IN THE ELKHORN MOUNTAINS, MONTANA

HARRY W. SMEDES

U. S. Geological Survey, Spokane, Washington

Sills are abundant in the Late Cretaceous, pre-Boulder Batholith intrusive sequence in the Elkhorn Mountains in west central Montana. They comprise basalt, lamprophyre, andesite, diorite, and granodiorite—with andesite and basalt prevailing—and are as much as 2,000 feet thick.

In strata of Belt and Paleozoic age, true sills are most abundant; injection dilation is the important mechanism of emplacement and enclosing shales are often contorted. In Cretaceous sedimentary rocks, intrusives tend to have concordant bases but partly discordant tops with irregular upwellings and dike offshoots. Injection dilation was accompanied or followed by stoping and assimilation along the top.

In Upper Cretaceous volcanic rocks, sills occur largely as apophyses of larger plutons, are wedge shaped and commonly divergent by forking or changing intrusion horizon. Depth of cover was slight.

In pre-volcanic rock strata, argillaceous horizons were preferred; in the volcanic rocks, true sills abound in bedded water-laid volcanic mudstones and siltstones, and welded tuffs. In coarser, poorly bedded pyroclastics, diverging sills prevail; in volcanic breccias, sills have gradational, ill-defined contacts masked by country-rock recrystallization and local assimilation.

A unique sill type in some water-laid bedded volcanic sedimentary rocks exhibits intimate mixing of country-rock with thick marginal zones of amygdaloidal igneous rock, each retaining its own characteristics even on a microscopic scale. Observations of dike offshoots from the basal amygdaloidal zone cutting through the sill support the hypothesis that these zones acquired water from moist semi-consolidated sediments, enabling them to remain mobile. Assimilation was very slight and the roof gently deformed.

ORIGINAL RADIOGENIC LEAD, AN ADDITIONAL CORRECTION FOR LEAD-URANIUM AND LEAD-LEAD AGE CALCULATIONS

L. R. STIEFF AND T. W. STERN

U. S. Geological Survey, Washington, D. C.

The age of uranium ore minerals can be determined from the Pb^{206}/U^{238} , Pb^{207}/U^{235} , and Pb^{207}/Pb^{206} ratios. In general the following sequence of ages results: Pb^{206}/U^{238} youngest, Pb^{207}/U^{235} slightly older, and Pb^{207}/Pb^{206} much older than both lead-uranium ages. Wickman has attributed this sequence of ages to the much greater loss of radon compared to actinon, gaseous daughter products in the U^{238} and U^{235} series, respectively. Some investigators prefer the Pb^{207}/U^{235} age because it is essentially unaffected by loss of actinon.

Possible alteration and the loss of uranium or lead, or both, have led some recent investigators to choose the Pb^{207}/Pb^{206} age. This age calculation should be satisfactory if corrections for radon loss, original lead, and mass spectrometric errors are small.

Kovarik and others have mentioned that the absence of original radiogenic lead is a necessary condition for satisfactory age determinations. Recent studies on lead minerals and uranium ores from the Colorado Plateau province have shown that these uranium ores contain at least two generations of radiogenic lead: original radiogenic lead deposited with the uranium and radiogenic lead formed after deposition by the decay of the uranium. The correction of Plateau uranium ores with the average isotopic composition of Plateau lead minerals still results in a large discrepancy between Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages. Added corrections for the isotopic composition of the original radiogenic lead, which has also been

found in certain Colorado Plateau province lead minerals, bring the $\text{Pb}^{206}/\text{U}^{238}$, $\text{Pb}^{207}/\text{U}^{235}$, and $\text{Pb}^{207}/\text{Pb}^{206}$ ages into agreement within limits of experimental error.

RADIOCARBON MEASUREMENTS AT THE U. S. GEOLOGICAL SURVEY

HANS E. SUESS AND MEYER RUBIN

U. S. Geological Survey, Washington, D. C.

During the past year a method for C^{14} determination has been developed and applied at the Geological Survey in Washington. Employing acetylene as a counting gas, the method extends the age limit for radiocarbon dates to almost 40,000 years. So far, about 100 dates have been obtained by this method. Our main object has been the dating of pre-Mankato material and the establishing of an absolute time scale for glacial events in the later part of the Wisconsin age. The results show for example that a major glacial advance took place in North America about 20,000 years ago, penetrating in certain areas farther south than any previous glacier in the Wisconsin age.

Further investigations were made on general questions such as the suitability of carbonate samples for dating.

GEOCHEMICAL ASPECT OF THE VOLCANIC ROCKS OF CIENEGA, NEW MEXICO*

MING-SHAN SUN AND BREWSTER BALDWIN

New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico

Six main volcanic units occur at Cienega, 15 miles southwest of Santa Fe, N. M. Andesite breccia, resting on late Eocene Galisteo formation, was domed by monzonite, which in turn was eroded and buried by calcic and glassy latite breccia and Cieneguilla limburgite. Pleistocene gravel and basalt bevel this sequence.

Refractive indices of 80 fused samples, ranging from 1.525 to 1.646, reflect the silica content, ranging from 69.04% to 38.99%. Spectrographic analyses show that nickel, vanadium, and chromium vary inversely with silica content.

The rock standard cells, derived from complete chemical analyses by methods of Barth and Eskola, are presented in the following modified Holmquist chemical formulae:

Glassy latite: $\text{Si}_{61.59}\text{Al}_{18.20}\text{Fe}_{2.45}^{3+}\text{Fe}_{0.40}^{2+}\text{Mg}_{0.66}\text{Ca}_{3.24}\text{Na}_{8.53}\text{K}_{4.37}\text{Ti}_{0.38}\text{P}_{0.12}\text{Mn}_{0.06}$

$[\text{O}_{162.26}(\text{OH})_{7.56}]_{169.82}$

Monzonite: $\text{Si}_{57.22}\text{Al}_{18.14}\text{Fe}_{3.73}^{3+}\text{Fe}_{0.68}^{2+}\text{Mg}_{1.76}\text{Ca}_{5.79}\text{Na}_{7.16}\text{K}_{4.69}\text{Ti}_{0.47}\text{P}_{0.23}\text{Mn}_{0.13}$

$[\text{O}_{159.40}(\text{OH})_{7.22}]_{166.67}$

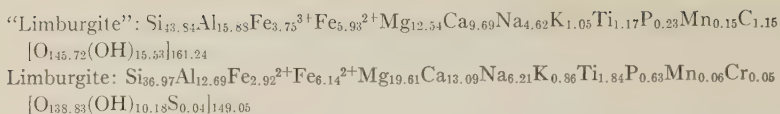
Calcic latite: $\text{Si}_{52.26}\text{Al}_{19.20}\text{Fe}_{5.32}^{3+}\text{Fe}_{0.97}^{2+}\text{Mg}_{2.58}\text{Ca}_{6.60}\text{Na}_{7.48}\text{K}_{4.57}\text{Ti}_{0.60}\text{P}_{0.41}\text{Mn}_{0.06}$

$[\text{O}_{154.38}(\text{OH})_{10.68}]_{165.06}$

Basalt: $\text{Si}_{47.92}\text{Al}_{16.37}\text{Fe}_{3.12}^{3+}\text{Fe}_{3.67}^{2+}\text{Mg}_{9.07}\text{Ca}_{9.40}\text{Na}_{6.01}\text{K}_{2.49}\text{Ti}_{1.08}\text{P}_{0.85}\text{Mn}_{0.12}$

$[\text{O}_{148.83}(\text{OH})_{13.92}]_{162.75}$

* Publication authorized by the Director, New Mexico Bureau of Mines and Mineral Resources.



The total number of anions, including hydroxyl and non-oxygenous anions such as sulphur, is directly proportional to cation number of Si. The number of Ti increases with decrease of Si.

ARDENNITE FROM THE GRANTS URANIUM DISTRICT, NEW MEXICO*

MING-SHAN SUN AND ROBERT H. WEBER

New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico

Ardennite, a hydrous silicate of manganese, aluminum, and vanadium, has been found as a rare associate of Plateau-type uranium minerals about 20 miles northwest of Grants, New Mexico. The mineral occurs as rosettes of tapered, acicular crystals that coat a nearly vertical joint surface in Jurassic Todilto limestone. Recrystallized calcite underlies, and is partly intergrown with the ardennite rosettes. Cuprosklodowskite occurs as sparse, small flecks on ardennite.

Rosettes about 2.8 mm. in diameter consist of radially disposed prismatic crystals approximately 0.3 mm. (*a*-axis) \times 0.07 (*b*-axis) \times 1.3 mm. (*c*-axis). *b*-faces are especially prominent in a few crystals. Cleavage is 010 perfect, and 110 distinct. Color black. Streak brown. Luster subadamantine. Very brittle. Pleochroism dark reddish brown to yellowish brown, with absorption $X > Y > Z$. $X = c$. $a = 2.01$ by immersion method. Dispersion distinct. Readily fusible in alcohol flame to a dull black bead.

X-ray analyses by both Laue and rotation methods indicate an orthorhombic symmetry, with cell dimensions: $a_0 = 9.201 \text{ \AA}$, $b_0 = 30.023 \text{ \AA}$, $c_0 = 6.280 \text{ \AA}$. Previous data by Gossner and Strunz gave: $a = 18.56 \text{ \AA}$, $b = 5.83 \text{ \AA}$, $c = 8.72 \text{ \AA}$.

Major constituents, determined by spectrographic methods, are Mn, Al, V, Fe, and Si. Minor constituents are Ca 0.1–1.0%, Na trace, Co 200 ppm, Ni 20 ppm, Ba 100 ppm, Sr 300 ppm, and Pb 100 ppm.

ISOTOPIC COMPOSITION OF LEAD IN OLIVINE BOMBS

C. R. TILTON, C. C. PATTERSON, AND G. L. DAVIS

Dept. of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D. C.
 California Institute of Technology, Pasadena, California; Geophysical Laboratory,
 Washington, D. C.

Two laboratories have conducted independent studies of the isotopic composition of lead in three olivine bombs of Quaternary age. Diopside separated from a bomb from Dreiser Weiher, Germany, contained 2 parts per million lead with an isotopic composition of $206/204 = 19.5$, $207/204 = 15.5$, $208/204 = 39.7$. The uranium content of the diopside was determined by isotope dilution to be 0.0067 parts per million. Lead in the diopside of

* Publication authorized by the Director, New Mexico Bureau of Mines and Mineral Resources.

a second bomb from San Bernardino, California, had a concentration of 2 parts per million and an isotopic composition almost identical with that of the Dreiser Weiher bomb. An olivine bomb from the western branch of the 1800 flow, Hualalai Volcano, Hawaii, contained 1 part per million lead in the composite bomb with an isotopic composition of $206/204 = 19.29$, $207/204 = 15.45$, $208/204 = 37.95$.

These data indicate that the lead in the bombs has spent most of its past history in an environment with a much higher ratio of uranium to lead than that found in the bombs today. The uranium now in the diopside of the Dreiser Weiher bomb would have changed the 206/204 ratio of its lead by only 0.7 per cent in the past 4.5 billion years. Because of this evidence of extreme differentiation, we believe that the bombs may not be representative of the chemical composition of their source materials.

The leads in all three bombs show abnormally high 206/204 ratios relative to their respective 207/204 ratios when compared to the average young ore lead. This could be explained as contamination by young, or lately formed radiogenic lead, although it is difficult to envisage a mechanism for such a process.

SYNTHESIS OF THE HUMITES

A. VAN VALKENBURG, JR.

National Bureau of Standards, Washington, D. C.

The humites are neosilicates of magnesium containing fluorine and hydroxyls. Their general formula is expressed as $n\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{F}, \text{OH})_2$ in which $n = 1$, norbergite, 2 chondrodite, 3 humite and 4, clinohumite. Fluorine end members have been synthesized from melts and solid state reactions. No success was obtained in synthesizing compositions where n was greater than 4 or less than 1. The humite synthesis using hydrothermal techniques has been accomplished and partial substitution of OH for F has been achieved. No completely hydroxyl end member of the series has been synthesized and it is concluded that none exists. Data based on phase determinations using quench techniques indicate the fluorine end members are an incongruent melting series. The optical constants of the fluorine end members are:

	α	β	γ	2V
Norbergite	1.548	1.552	1.570	33°
Chondrodite	1.582	1.594	1.612	50°
Humite	1.598	1.606	1.630	59°
Clinohumite	1.608	1.618	1.636	76°

The x-ray powder data of the synthetic humites agrees well with the recent published work on natural humites by T. G. Sahama.

WALLROCK ALTERATION IN THE BROKEN HILLS RANGE, NEVADA

CHARLES J. VITALIANO

Indiana University, Bloomington, Indiana

Investigation of a "talc" deposit which gave high Al_2O_3 analyses showed considerable quantities of associated sericite and chlorite. The deposit occurs north of Gabbs, Nevada, in the Broken Hills range, and is the result of wallrock alteration of a rhyolite porphyry along a vertical fissure.

Chemical analyses show an increase of MgO and a correlative decrease of SiO_2 , Al_2O_3 , K_2O and Na_2O across the alteration zone towards the fissure. Thin section study shows an

orderly selective replacement of biotite, feldspars and quartz in the host rhyolite. Introduced minerals are sericite, green chlorite flakes, sericite (second stage), talc, tourmaline and chlorite in fine-grained aggregates.

Alteration was the result of MgO-bearing hydrothermal solutions moving upwards along the fissure and outwards into the wallrock. With the exception of tourmaline, the alteration minerals are built up of certain layer type lattice units. The formation of any of the above alteration minerals reflects the availability of the proper basic layer lattice unit at that particular time. Some of the necessary basic layer lattice units became available during the process of destruction of the host minerals; others, particularly the brucite lattice were formed from components introduced in solution. The more mobile elements (Na_2O , K_2O) were removed in solution.

POSSIBLE REACTION AND EUTECTIC RELATIONS BETWEEN NATURALLY OCCURRING FELDSPARS FROM THE JUDITH MOUNTAINS, MONTANA*

STEWART R. WALLACE

U. S. Geological Survey, Denver Federal Center, Denver, Colorado

Rocks containing two primary alkali feldspars are rare. Recent investigations by Bowen and Tuttle of the system $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 - H_2O indicate that the alkali feldspars form mixed crystals at high temperatures (in anhydrous melts), but that a sufficient pressure of water vapor will depress the solidus-liquidus curves below the solvus and result in the formation of two feldspars, first by a reaction relation, and, at still higher pressures and lower temperatures, by a eutectic relation.

Vesicular and brecciated textures of intrusive alkali syenite, alkali rhyolite, and tinguaitite breccia suggest that their corresponding magmas contained abundant volatiles. Albite, An_5 , phenocrysts with reaction rims of potash feldspar suggest that the volatile content depressed the crystallization temperature of the feldspars to the reaction point.

Exceptionally large doubly-terminated crystals of quartz in an alkali granite porphyry stock on Judith Peak are, in spite of their habit, probably low quartz and suggest growth in a fluid magma at a relatively low temperature. Silicification of the wall rock and granitization of sedimentary rock inclusions indicate an exceptionally high concentration of volatiles. Textural and size relationships of both sanidine and albite, An_3 , crystals in an early fine-grained facies of the alkali granite and a later coarse-grained facies suggest simultaneous growth of both feldspars and implies a eutectic relation.

The relationship of these feldspars may illustrate in magmas both the reaction and eutectic relations between the alkali feldspars postulated by Bowen and Tuttle on the basis of their laboratory investigation of hydrous melts.

$\text{A}^{40}\text{-K}^{40}$ DATING METHOD

G. J. WASSERBURG AND R. J. HAYDEN

Institute for Nuclear Studies, University of Chicago; Argonne
National Laboratory, Lemont, Illinois

The radiogenic argon content of several potassium feldspars of known lead-uranium age has been determined using an isotopic dilution technique. Using a branching ratio of 0.085 and a decay constant of $\lambda = 0.55 \times 10^{-9} \text{y}^{-1}$, it was found that the calculated $\text{A}^{40}/\text{K}^{40}$ ages could be brought into agreement with the Pb-U ages within 6%. The good agreement

* Publication authorized by the Director, U. S. Geological Survey.

which was obtained for different samples ranging in age from 260 million to 1,000 million years indicates no serious loss of argon by diffusion in feldspars.

The A^{40}/K^{40} age of a sample of Beardsley meteorite, a gray chondrite, has been determined. The value obtained was 4.8×10^9 years using the above listed constants. The determination of potassium in Beardsley was made using an isotopic dilution technique with K^{41} tracer obtained from Oak Ridge. The material was analyzed using a surface ionization technique.

X-RAY DIFFRACTOMETER THERMAL STUDIES OF CLAY-MINERAL DEHYDROXYLATION

E. J. WEISS¹ AND RICHARDS A. ROWLAND²

¹Department of Ceramic Engineering, The University of Texas; Consultant to Exploration and Production Research Division, Shell Development Company, Houston, Texas, and ²Exploration and Production Research Division, Shell Development Company, Houston, Texas

With an oscillation-heating x-ray diffraction technique the position and intensity of an x-ray diffraction maximum may be followed continuously while a powdered sample is heated at a regular rate of temperature rise (5° C. per minute). The sample is sedimented on a platinum slide mounted in a furnace designed to fit the horizontal shaft of the North American Phillips x-ray Diffractometer. The diffractometer is set with the maximum to be followed at the center of a one-half degree 2θ oscillation. After heating and oscillating the tops of the recorded series of peaks indicate position and intensity. The bottoms represent the background which is very sensitive to position changes.

Typical oscillation-heating patterns of basal spacing maxima for Georgia kaolinite, a Vermont chlorite, a clinocllore, and sheridanite are presented. The kaolinite (001) remains constant at 12.5 2θ until it collapses at 525° C. The chlorites (002) shift from 12.51° 2θ to 12.47° 2θ and begin to collapse simultaneously with the intensity increase of the (001).

Sheridanite (001) increases abruptly at 525° C. and collapses at 750° C. after shifting from 6.28° to 6.49° 2θ . Clinocllore follows a similar pattern. The (002) collapses abruptly at 525° C. Vermont chlorite (001) begins the intensity increase at 500° C., is greatest at 640° C., begins to collapse at 740° C. and is collapsed at 810° C. after shifting from 6.28° 2θ to 6.52° 2θ . The (002) collapse begins at 500° C. and is complete at 810° C. These differences may be related to the iron content of the brucite layer.

HARDNESS DETERMINATIONS ON SILICON, GERMANIUM, AND THE III-V COMPOUNDS

G. WOLFF, L. TOMAN, JR., N. J. FIELD, AND J. BRODER

Chemical Physics Branch, Squier Signal Laboratory, Fort Monmouth, New Jersey

Micro-indentation hardness measurements have been made on certain substances with diamond and sphalerite type structures using a Knoop type diamond indenter. The investigation, performed mainly on {111} planes (or {1 $\bar{1}$ 1} planes), showed differences in hardness for different directions and, to a lesser extent, for different areas. Since the hardness varied slightly for identical crystallographic directions and localized areas, the data were evaluated statistically. The plots of the indentation values for all substances investigated gave straight lines on probability paper. This indicates a normal Gaussian distribution of the data. The Knoop hardness values, derived from $H = CL/l^2$ (C-constant, L-load applied to indenter, l-length of indentation), range from 83 to 190 (Mohs values from 2½ to 5) for the III-V compounds (InSb, InAs, InP, GaSb, GaAs, GaP, AlSb, AlAs), and from 268 to 547 (Mohs values from 4½ to 6) for germanium and silicon. These values are roughly proportional to r^{-8} , where r is the inter-atomic distance.

ALMANDITE GARNET STABILITY RANGE

HATTEN S. YODER, JR.

Geophysical Laboratory, Washington, D. C.

The upper thermal stability limit of almandite garnet, $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, has been determined up to 10,000 bars water vapor pressure. The univariant equilibrium curve for the reaction



passes through the points 1030° C.—10,000 bars; 980° C.—8000 bars; 930° C.—6000 bars; 880° C.—4000 bars; and 830° C.—2000 bars. A projection of this curve indicates that almandite would be stable below 785° C. at atmospheric pressure.

The synthetic almandite crystals are cinnamon brown in color and exhibit the dodecahedral and icositetrahedral forms usually, and the cube and octahedron rarely. They are optically isotropic with $n = 1.830 \pm 0.003$ in sodium light. The powder x-ray diffraction pattern is identical with that of a natural almandite close to the ideal composition and has $a_c = 11.53 \pm 0.01 \text{ \AA}$.

Growth is obtained from glass ($n = 1.662$) of the requisite composition and a mix consisting of ferrous oxalate dihydrate, gamma alumina, and silica glass. Complete reaction is obtained in less than two hours at the highest pressures and temperatures, and the rate of reaction falls off rapidly below 7000 bars to nil at 1000 bars. Oxidation of the breakdown products to magnetite + quartz + hercynite, magnetite + iron—cordierite + hercynite, or to magnetite + quartz + corundum is common.

The occurrence of almandite in the metamorphic rocks as well as in some igneous rocks is accounted for by the character of the stability curve. The behavior of these garnets in the "wet" and "dry" contact aureoles can also be interpreted from the experimental data.

FACTORS INFLUENCING THE ARTIFICIAL PRECIPITATION OF CALCIUM CARBONATE

EDWARD J. ZELLER AND JOYN L. WRAY

University of Wisconsin, Madison, Wisconsin

Aragonite, calcite, and vaterite have been precipitated under conditions of controlled temperature, pH, and impurity ion concentration. Results from x-ray diffraction studies, spectrographic analysis, microscopic examination, and thermoluminescence studies have provided information regarding the extent to which these three factors effect the formation of the various crystalline forms. CaCO_3 precipitates were made from dilute solutions of $\text{Ca}(\text{NO}_3)_2$ by the controlled addition of dilute Na_2CO_3 .

Employing this method of precipitation, high pH, high concentrations of Pb^{++} , Sr^{++} , Ba^{++} , low concentrations of Mg^{++} , and a temperature range from 50° to 65° C. appear to favor aragonite formation. However, aragonite was produced at temperatures outside this favorable range when conditions of high pH and favorable impurity concentration existed. Calcite and vaterite have been obtained throughout a wide temperature range. Calcite formation is favored by a lower pH, low concentrations of Pb^{++} , Sr^{++} , Ba^{++} , and high concentrations of Mg^{++} . pH and impurity effects cannot easily be correlated directly with the synthesis of vaterite.

pH and impurity effects are closely related and appear to be significant factors influencing the crystalline form of CaCO_3 . Temperature influences the crystalline form of the precipitate primarily through its effects upon pH and the solubility of the impurity ions. The conclusion that impurities are the controlling factors determining the crystalline form of CaCO_3 under conditions of constant temperature is supported by evidence obtained from spectrographic studies of natural cave formations.

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, November 4th, 1954, at 5 P.M., in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission).

The following papers were read:

- (1) *The determination of composition and thermal history of plagioclase by the x-ray powder method*

By J. GOODYEAR AND W. J. DUFFIN

Heat-treatment of eight natural plagioclases covering the composition ranges 0–65% and 80–100% anorthite is found to produce changes in the x-ray powder patterns which indicate that states of partial inversion are possible.

In the range 0–65% anorthite, the changes which take place as anorthite content increases are identical with those occurring on heat-treatment, and this limits the assignment of a definite composition and thermal history to a plagioclase in this range on the basis of its powder pattern alone.

In the range 80–100% anorthite, composition can be obtained from x-ray data without a knowledge of thermal history, and an estimate can then be made of the degree of inversion.

- (2) *A note on albite twinning in plagioclase feldspars*

By P. GAY

Previous work by Donnay on the basis of the geometrical theory of twinning related the width of albite twin lamellae to the composition of the plagioclase. The curve derived by Donnay has been recalculated for both high and low feldspars from x-ray data; the two curves differ markedly only in the region between 0 and 20% Ab. Some experimental evidence supporting the deductions which can be made is given.

- (3) *Experimental and theoretical studies of the mica polymorphs*

By J. V. SMITH AND H. S. YODER, JR.

An experimental and theoretical study has been made in order to determine the number and the structure of the possible polymorphs and to determine the structural relations between them. The simplest structures are $1M$, $2M_1$, $2M_2$, $3T$, $2O$ and $6H$ polymorphs and more complicated types can be developed. Some of the previously described polymorphs were not contained in the theoretical list and were re-examined. The $6M$ structure was found to be a $2M_2$ polymorph, the 6-layer triclinic type was found to be a $2M_1$ polymorph, and the $3M$ structure was shown to be a $3T$ type. The 24-layer triclinic structure could be described on a simpler 8-layer cell. This type together with a new 12-layer monoclinic structure, as well as other structures of higher periodicity, presumably consists of complex stacking and results from spiral-growth mechanism. Two extreme types of layer-disordered crystals may be built and a disorder of individual ions may also occur. Single stacking faults result in twinned crystals. A new twin relation (180° rotation about the $[100]$ axis) has been recognized.

Twenty specimens from extreme geological environments have been examined in order to evaluate the control of environment on the stacking. The type of stacking could not be attributed solely to the influence of pressure and temperature. Composition appears to play a dominant role in the type of stacking and semi-quantitative structural arguments appear to support this contention. The influence of growth mechanism is discussed.

A scheme for the identification of the mica polymorphs by *x*-ray powder and single-crystal methods is given.

- (4) *The hydration of larnite (β -Ca₂SiO₄) and bredigite (α ₁-Ca₂SiO₄) and the properties of the resulting gelatinous mineral plombierite*

By J. D. C. McCONNELL

An account is presented of the hydration of larnite and bredigite as observed in contact metamorphic rocks from Ballycraig, Larne, N. Ireland. The results are also given of a detailed study of plombierite, the gelatinous hydration product of the natural dicalcium silicates.

The mechanics of the hydration process and of gel formation from β -Ca₂SiO₄ in hydrating portland cement are discussed.

- (5) *A suggested igneous origin for the banded granular hornfelses within the hypersthene-gabbro of Ardnamurchan, Argyllshire*

By G. M. BROWN

The development of the banded granular hornfels inclusions within the hypersthene-gabbro of Ardnamurchan has recently been attributed to the metasomatism of sediments, the evidence being textural and compositional. It is suggested that such evidence favors, rather, the thermal metamorphism of layered basic or ultrabasic igneous rocks.

The following papers were taken as read:

- (1) *The occurrence of palygorskite near Ipswich, Queensland*

By L. E. ROGERS, A. E. MARTIN, AND K. NORRISH

The mineral palygorskite has been found associated with dolomite in the Ibis Dolomite Quarry near Mt. Flinders, Queensland. *X*-ray, chemical and thermal methods were used to identify the mineral. The palygorskite occurs pure and mixed with dolomite and other minerals. It was also found as a dominant mineral of the cores from a bore situated (at Cribb's Estate), about 17 miles from the above quarry, suggesting that palygorskite occurs extensively in the area. A systematic study of the area would probably reveal clay deposits suitable for commercial use. The dolomite and palygorskite may have been formed in freshwater lakes which existed between successive Tertiary basalt flows. Sepiolite occurs as hard cores in the clayey palygorskite veins; it is suggested that palygorskite is an alteration product of sepiolite.

- (2) *An accessory to the polarizing microscope for the optical examination of crystals*

By H. C. G. VINCENT

A sphere, with the crystal grain mounted at its centre, rotates upon a triple support, allowing selection of orientation. When measurements are required, a direction, such as that of an optic axis in the interference figure, is adjusted to the cross hairs of the microscope and the corresponding point of emergence is plotted on the sphere itself by means of an automatic marking device. Great circle distances between points thus plotted may be measured, and angles may be set off, by simple methods described, and auxiliary stereographic projection is unnecessary. The sphere with plotted data represents a working model of the indicatrix of the mounted crystal, furnishing cardinal observation directions for refractive index and other optical determinations.

(3) *Rammelsbergite from the southern uplands of Scotland*

By A. K. TEMPLE (communicated by W. Q. KENNEDY)

Rammelsbergite as thin borders on niccolite (this on galena), from the Glencrieff mine, Wanlockhead, has been identified by the x-ray powder spacings and by etching tests. Three doubtful occurrences in the southern uplands are mentioned.

(4) *The significance of tridymite in igneous and metamorphic petrogenesis*

By G. P. BLACK

The presence of tridymite in a rock indicates that relatively low pressures obtained during its formation. Closer limits to the pressure and hence to the depth of formation can be estimated when some other pressure- or temperature-indicating mineral is associated with tridymite. The maximum thicknesses of cover under which various tridymite-bearing members of the Tertiary complexes of Skye, Rhum, and Ardnamurchan were emplaced can be determined in this way; in the case of the Khum complex, the thickness of cover consistent with the physico-chemical data is shown to have been less than 3850 and probably less than 2650 metres, figures very much lower than the 8500 metres recently envisaged by Wager (1953).

(5) *Rodingite from the Girvan-Ballantrae complex, Ayrshire*

By T. W. BLOXHAM

Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary.)

SUMMARIES OF PAPERS PRESENTED BEFORE THE CLAY MINERALS GROUP OF THE
MINERALOGICAL SOCIETY (LONDON), NOV. 5, 1954J. ENDELL: *Clays in coals and their ashes*

Clay minerals occurring in brown and bituminous coals have been identified by x-rays as illites and kaolinites. These are the constituents of primary ashes, i.e., the minerals originally associated with the coals. Besides these there are the secondary ashes, formed from inorganic constituents, such as lime and sulfides, on burning the coal. The reaction between the clay minerals and the other constituents in ash formation is described, as well as the influence of clays in coking and on slag formation. Clays raise the viscosity of slags. In bituminous coals the setting point is raised and in brown coals lowered by the presence of clays. Examples in industrial firing practices are given.

P. GALLITELLI: *Mineralogical composition of some clays of the clay-schist formation in the Modenese Apennines*

Examination of some of the above clays from Varana, Sassamorello and Castelveccchio has been carried out using usual optical, x-ray, and differential thermal methods. The clays examined contain illite, a kaolin mineral, and chlorite, and have the following characteristics: (a) the kaolin mineral is poorly crystallized; (b) the illitic mineral is highly hydrated; (c) the chloritic mineral has a mixed-layer structure with random interstratification of a swelling layer—being similar in some respects to minerals previously described as occurring in England and in Germany; (d) the sand fraction contains small amounts of basic glass of andesitic type.

P. FRANZEN: *X-ray analysis of an adsorption complex of montmorillonite with cetyltrimethyl ammonium bromide (lissolamine)*

The method of van Olphen for determination of the cation-exchange capacity of small samples of clays uses lissolamine and is based on the fact that at the equivalence point

the clay is simultaneously oleophilic (at the micelle surface) and hydrophilic (at the micelle edges) and therefore can act as an excellent emulsifier for oil-water systems. X-ray analysis has confirmed the adsorption of lissolamine ions. It has proved possible, however, to adsorb still more lissolamine, in quantities up to 2.4 times the cation-exchange capacity. The x-ray powder photographs of this adsorption complex show a large number of orders of the basal reflection, and enable its general structure to be evaluated.

R. GREENE-KELLY: *An unusual montmorillonite complex*

A highly regular complex of pyridine and montmorillonite with a basal spacing of 23.3 Å has been investigated by one dimensional Fourier syntheses, and the structure has been partly determined. The effect on the stability of the complex of traces of water, the nature of the exchange cation, and the substitution of pyridine by picolones is discussed.

P. MURRAY AND J. WHITE: *A kinetic study of the dehydration reaction in clays and its bearing on differential thermal analysis*

The isothermal decomposition of several clays has been investigated and it has been found that the decomposition can be treated to a first approximation as a first order reaction. Rate constants and energies of activation for the reaction have been evaluated. The results have been used to predict the form of the thermal analysis peak and the effect of heating rate upon it. An attempt has been made at a formal analysis of the results in terms of the theory of rate processes.

E. B. ALLISON: *The determination of specific heats and heats of reaction of clay minerals by thermal analysis*

Vold's mathematical analysis of the *d.t.a.* curve has been applied to Murray's thermal data on the dehydration of clay minerals. Owing to experimental uncertainties, values for heats of dehydration are lower than those determined by other methods. The first order law is obeyed and activation energies of dehydration are of the same order as those derived from other data; rates of dehydration are, however, higher. Smith's constant-heat-flow method has been used to determine specific heats and heats of dehydration of clays, and the effects of sample porosity upon the results has been determined. The thermal data is also used to estimate the amount of clay mineral present. The kinetics of the dehydration process evaluated from the *apparent specific heat-temperature* curves follow a first-order-reaction curve. The activation energies obtained are, however, higher than those derived from other data.

F. VAUGHAN: *Energy changes when kaolin minerals are heated*

Activation energies have been experimentally determined for the dehydration of various kaolin minerals. The fireclay mineral is distinctive and it is suggested that it does not form part of a halloysite-kaolinite series. It is further thought possible that there is a series of fireclay minerals. From thermochemical and thermodynamic considerations the heat of formation of kaolinite has been approximately calculated. Estimated enthalpy and free energy changes for the exothermic reaction at 980° C. indicate that, if a compound is produced during dehydration, the most probable explanation of the exothermic reaction is the simultaneous production of mullite, γ - Al_2O_3 and SiO_2 . Finally, the lattice energies of kaolinite and its thermal decomposition products have been calculated.

E. C. SEWELL: *The consequences for d.t.a. of assuming a reaction to be first-order*

Isothermal experiments of Murray and White led to the conclusion that the dehydration reactions of clays are first-order. The problem of a specimen heated at a constant rate

throughout is recalled, particular attention being drawn to the effect of heating rate on the temperature at which the maximum rate of reaction occurs. To apply to *d.t.a.*, this analysis must be extended to take account of thermal gradients. The most important result concerns the effect of the size of the specimen and of dilution on the position of the turning-point. A disagreement with the results of experiments on kaolinite is pointed out and it is argued that only a small part of this disagreement is due to simplifications made in developing the theory. It is concluded that the hypothesis that the clay reactions are first-order is only approximate.

R. F. YOELL: *Chamosite variability and iron-ore petrology problems*

There appears to be a variation in composition and perfection of crystallization of chamosite with the source from which it is extracted. Specimens from the Northamptonshire Sand Ironstone show that all the chamosites from the Main Oolitic Ironstone are of the ordered hexagonal type with high iron content, while all chamosites from the Chamosite-Kaolinite beds are of the disordered form with lower iron content. Enrichment of the Chamosite-Kaolinite beds subsequent to deposition has in some areas rendered them indistinguishable from the plain Ironstone beds, and it has been very difficult to delineate the two deposits. An attempt has been made to use the chamosite type as a "label" for differentiation in ores from the Easton Neston area.

G. BROWN: *The effect of chemical composition upon (00l) intensities of micas and chlorites*

In the micas (including illites) variations in diffracted *x*-ray intensities occur due to differences in the octahedral cations and in the interlayer cations, and the calculations deal with the compositions which lie within the field whose corner members are: $K_2(Al, Si)_8(Al_4)O_{20}(OH)_4$, $K_2(Al, Si)_8(Fe_4)O_{20}(OH)_4$, $(H_2O)_2(Al, Si)_8(Al_4)O_{20}(OH)_4$ and $(H_2O)_2(Al, Si)_8(Fe_4)O_{20}(OH)_4$. Similar calculations have been made for trioctahedral micas. In the chlorites the composition of both the talc sheet and the brucite sheet can vary. The intensities of the (00l) reflections of chlorites with compositions between $(Mg_{12})(Si, Al)_8O_{20}(OH)_{16}$ and $(Mg_4Fe_8)(Si, Al)_8O_{20}(OH)_{16}$ have been calculated allowing for both symmetrical and asymmetrical distribution of the octahedrally coordinated cations between the two types of octahedral sites.

R. C. MACKENZIE, *Hon. Secretary*

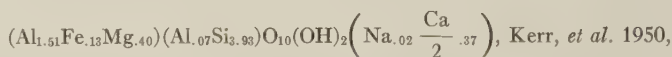
NOTES AND NEWS

OXIDATION OF MONTMORILLONITE DURING LABORATORY GRINDING

W. D. KELLER, *University of Missouri, Columbia, Missouri.*

Oxidation of iron in montmorillonite may occur sufficiently during laboratory grinding of the clay to be observable by simple tests. This reaction appears to be important in implications beyond the simple laboratory experiment.

The Cheto (Chambers), Arizona, bentonite is well known because of its extensive use in industry. When freshly mined, it is a grayish white clay containing scattered fine, dark gray spots. Although it is a relatively pure Ca-montmorillonite



it does not stain blue when benzidine solution is applied to the lumps. The fact that it does not react with benzidine is not unique, because Page (1941) pointed out long ago the unreliability of the benzidine reaction for identification of montmorillonite. He showed that benzidine is oxidized to a blue compound by an ion which transfers a single electron, that the blue stain is really an indicator of an oxidant, and that available ferric ions, which are likely to occur in nature, are notably efficient oxidants of benzidine to the characteristic blue semiquinone.

Failure of the fresh Cheto lump clay to stain with benzidine indicates, therefore, the absence of available ferric ions. If the clay is pulverized by grinding in air for a few minutes with a laboratory mortar and pestle, it takes on a faint buff color which can be observed by comparing the lump and pulverized clays. This pulverized clay now stains a brilliant blue when wetted with benzidine solution. This reaction indicates the presence of available oxidizing ions, and the very light tan color suggests that iron in the clay has been changed to iron oxide which presumably is now effective in oxidizing benzidine to a blue substance. Several results and implications arise from the oxidation.

1. Another geologic example is given of the unreliability of the benzidine test for montmorillonite.
2. An oxidized outcrop of montmorillonite may stain with benzidine although the fresh clay may not.
3. By grinding montmorillonite and exposing more surface, tan-colored iron oxide is visibly formed.
4. It seems likely that the ferric-ferrous iron ratio would differ between lumps and pulverized material. How much this would affect analytical results is not known, but because analytical chemists ordinarily

pulverize clay samples prior to dissolving them, it is likely that error is introduced into the analysis by the sample preparation.

5. The appearance of a light tan color on the pulverized clay suggests (a) that ferrous iron in the octahedral layer of the clay crystal was exposed to the air and oxidized to ferric oxide, or (b) that ferric iron originally in symmetrical octahedral coordination with oxygen and hydroxyl within the octahedral layer suffered disruption of bonds on one side (asymmetrical) as it was exposed by grinding, and ferric oxide was formed.

In either case drastic changes in the crystal chemistry of the clay have occurred as more surface was exposed. These changes are probably of the same order of violence as occurs in some mineral inversions or replacements.

6. It seems probable that oxidized clay on an eroded outcrop may differ in physical and chemical properties from that occurring in the fresh interior. This is borne out by the observations of Williams, Elsley, and Weintritt (1953) who found in Wyoming bentonite, "The highest grade clay has a yellow color while the other type, a blue clay, is customarily found to be of lower grade. . . . The primary cause of variation in properties is due to the Na/Ca ratio in the exchange positions regardless of whether the iron in the clay is in the ferrous or ferric state."

7. Because the oxidized surface of the pulverized Cheto clay differs from the interior, it illustrates the principle that a reaction between an external medium and the surface of a reference mineral whose bulk composition is A_nB_m occurs actually with a surface whose composition is not A_nB_m . One wonders how significant this relationship (or difference) is in weathering, ore deposition, metamorphism, and other mineral reactions.

REFERENCES

- KERR, P. F., HAMILTON, P. K., AND PILL, R. J., A.P.I. Project 49, *Rpt. No. 7, Am. Pet. Inst.*, New York, p. 53 (1950).
PAGE, J. B., *Soil Sci.*, **51**, 133 (1941).
WILLIAMS, F. J., ELSLEY, B. C., WEINTRITT, D. J., *Abstracts, Second Conf. Clays and Clay Minerals, Natl. Res. Council*, p. 16 (1953).

HYDROHAUSMANNITE AND HYDROHETAEROLITE

A. D. WADSLEY*

Frondel (1953) recently described two new manganese oxide minerals one of which, hydrohausmannite $(\text{Mn}^{2+}, \text{Mn}^{3+})_{3-\delta}(\text{O}, \text{OH})_4$, although closely resembling hausmannite Mn_3O_4 , is differentiated by the presence of sev-

* Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.

eral per cent of water and some details in the x-ray powder pattern. From the cell dimensions, the structures of Mn_3O_4 and ZnMn_2O_4 (hetaerolite) are evidently similar, and a further close analogy may well exist between Frondel's new mineral and hydrohetaerolite which also contains "structural water" (Frondel and Heinrich 1942). The writer recently determined the crystal structure of hydrohetaerolite, and a brief discussion of the possible relations of the two minerals may be appropriate.

TABLE 1. X-RAY DATA FOR MANGANESE MINERALS WITH DEFORMED SPINEL STRUCTURE

	Hausmannite	Hetaerolite	Hydrohausmannite	Hydrohetaerolite
Cell dimensions in Å $\begin{cases} a \\ c \end{cases}$	$\begin{matrix} 5.75 \\ 9.42 \end{matrix}$	$\begin{matrix} 5.74 \\ 9.15 \end{matrix}$	$\begin{matrix} 5.79 \\ 9.49 \end{matrix}$	$\begin{matrix} 5.75 \\ 9.05 \end{matrix}$
Space group	$I4_1/amd$	$I4_1/amd$	—	$I4_1/amd$
Unit cell contents	$\text{Mn}_4^2\text{Mn}_8^3\text{O}_{16}$	$\text{Zn}_4\text{Mn}_8^3\text{O}_{16}$	Uncertain probably (Mn^{2+} , Mn^{3+}) $_{12-8}$ (O, OH) $_{16}$	$\text{Zn}_4\text{Mn}^{3+}_{6\frac{2}{3}}\text{O}_{12}(\text{OH})_4$
Reference	Aminoff (1919)	Frondel & Heinrich (1942)	Frondel (1953)	Wadsley (1954)

Hydrohetaerolite has the same structure as hausmannite, except that one sixth of the trivalent manganese occupying the octahedral sites are randomly absent, and the balance of charge is supplied by hydrogen bonds (Wadsley, 1954). The powder diffraction data for hydrohausmannite, indexed as body centred tetragonal with $a = 5.79$, $c = 9.49$ contains the strong line (002) at 4.65 \AA which distinguishes it from hausmannite. This reflection, however, is incompatible with the fourfold screw axis of the space group $I4_1/amd$ in which (00 l) can be present only if $l = 4n$. Although closely related chemically to hydrohetaerolite, the new mineral therefore possesses important crystallographic differences, an explanation of which may be sought in the following way.

It is well known that manganous hydroxide is rapidly oxidized, and Frondel (1953) found evidence of hydrohausmannite in several specimens of pyrochroite which had been exposed to the air. Pyrochroite has a layer structure, of which brucite (or cadmium iodide) is the typical member (Aminoff 1919). It consists of two-dimensional sheets of $\text{Mn}^{2+}(\text{OH})_6$ octahedra stacked so as to give hexagonal close packing of the anions in the adjacent layers which are held together by weak secondary forces. If we assume hydrohausmannite to be closely related to the tetragonal Mn spinels, and the cell dimensions leave little doubt about this,

it is clear that its formation from pyrochroite is a matter of considerable ease despite the apparent dissimilarity in atomic arrangement of the two structural types.

It is convenient for our purposes to picture the tetragonal spinel as a layer compound. Each of the planes represented by the form $\{101\}$ contains a brucite-type layer with every fourth octahedron regularly missing to form a hexagonal grouping. In one orientation the layers lie parallel in cubic close packing so as to form two kinds of interstitial sites, one tetrahedral, one octahedral. In the case of hausmannite, the tetrahedra coordinated to Mn^{2+} are located on each side of a layer and sharing the oxygens bounding a vacant octahedral site, the octahedra formed by Mn^{3+} are situated between triads of octahedra in adjacent layers and irrespective of position all sites are occupied. This is illustrated in Fig. 1. In hydrohetaerolite the vacancies are distributed at random over all the Mn^{3+} sites with certain reservations which are discussed elsewhere (Wadsley 1954).

The transformation of the brucite type lattice to that of niccolite (NiAs) may occur for the nonstoichiometric tellurides of Ni, Co, V, Ti and selenides of V and Ti (Ehrlich 1949, for a recent review) simply by

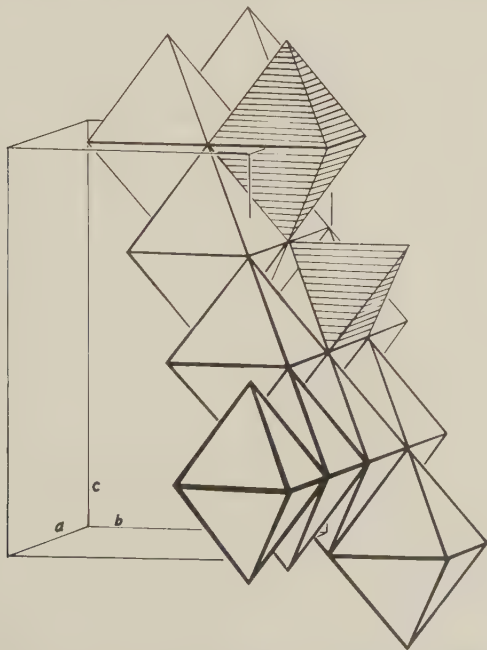


FIG. 1. The tetragonal spinel structure drawn (in part) as a layer of octahedra lying in the direction of the plane (011). The "interstitial" polyhedra are hatched, and for the sake of clarity only one of each type on only one side of the layer is drawn.

the interpolation of additional metal ions to the octahedral sites between the sheets with little change of symmetry or even of unit cell dimensions. In order to form a spinel however, the brucite structure must undergo three major changes:

- (a) The packing of the layers changes from hexagonal to cubic. The two unit cells, therefore, are not readily related by a simple matrix expression.
- (b) Every fourth metal atom leaves the sheet to take an interstitial position, Mn^2 tetrahedral, Mn^3 octahedral and possibly also tetrahedral. The analysis quoted by Frondel (1953) indicates that the oxidation has proceeded beyond that of hydrohetaerolite.
- (c) Oxidation occurs by the formation of ions of higher valency at the expense of hydrogen ions which presumably leave the structure as water molecules.

The oxidation of pyrochroite proceeds therefore by the migration of ions to their interlayer positions in the direction normal to (0001). It may be assumed that the tetrahedral positions are occupied first since no valence change is involved in the movement of Mn^2 ions. When the population of each octahedral interstitial site is equal to that of each site in the residual layer sheets (as in the case of hydrohetaerolite), the symmetry could correspond to 4_1 (or 4_3) and the layer structure is thereby completely destroyed. If incomplete, however, the atoms in the layers and in the interlayer sites are not present in equivalent amounts, and hence related by the fourfold screw axis in position but not in scattering power. Reflections (00*l*) for the unit cell with $l = 4n + 2$ could then occur, and as a consequence the symmetry although strongly pseudotetragonal would be lower. It is not possible without single crystal data to do other than speculate upon the space group, or lacking additional chemical analyses to determine the proportions of ions in the positions in the unit cell which correspond in the orientation given by Frondel to the spinel structure.

In a study of the formation of MgO crystallites by the dehydration of crystalline brucite, Garrido (1951) found that rapid heating induced supplementary spectra which he attributed to some periodicity of vacant lattice sites. It is possible therefore that the octahedral manganese atoms are completely equivalent only when the formation of hydrohausmannite is exceedingly slow, and also when the composition is analogous to that of hydrohetaerolite, i.e. $\text{Mn}^2\text{Mn}^{3}_{1\frac{2}{3}}\text{O}_3(\text{OH})$. Chemical studies of the oxidation of $\text{Mn}(\text{OH})_2$ indicated that synthetic hydrohausmannite is progressively oxidized to $\alpha\text{-MnO}(\text{OH})$ which is unrelated to manganite (Feitknecht and Marti, 1945) or to groutite. The x-ray powder pattern of $\alpha\text{-MnO}(\text{OH})$ indexed as tetragonal with $a = 8.3$, $c = 9.3 \text{ \AA}^*$ is again dominated by a line at or near 4.6 \AA .

* This is for the double face-centred cell. The body centred elements are $a = 5.9$, $c = 9.3 \text{ \AA}$.

Evidently therefore a complete non-stoichiometric series exists between the disordered hydrated oxides hydrohausmannite $\alpha\text{-MnO}(\text{OH})$ affording an interesting comparison with the anhydrous series $\text{Mn}_3\text{O}_4 - \gamma\text{Mn}_2\text{O}_3$ which is analogous to the better known $\text{Fe}_3\text{O}_4 - \gamma\text{Fe}_2\text{O}_3$ (Verwey and deBoer, 1936). The transition R_3O_4 to $\gamma\text{R}_2\text{O}_3$ is believed due to the oxidation of the metal ions R^2 to R^3 with concomitant vacant sites, the structure throughout being essentially that of spinel. For $\gamma\text{R}_2\text{O}_3$ one ninth of the metal atoms are randomly missing with no special distinction between tetrahedral or octahedral sites. However recent work on In_2S_3 , the high temperature form of which has the $\gamma\text{R}_2\text{O}_3$ structure indicated that vacancies were more frequent in the octahedral sites (Hahn and Klingler, 1949) as in hydrohetaerolite which we have seen corresponds to the R_3O_4 side of the series. One may therefore expect many intricate orderings within systems of this type, but a less speculative approach is hampered by the lack of specimens suitable for single crystal methods of structure analysis.

REFERENCES

- AMINOFF, G. (1919), *Geol. Fören. Förh.*, **41**, 407.
AMINOFF, G. (1926), *Zeits. Krist.*, **64**, 475.
EHRlich, P. (1949), *Zeits. Anorg. Chem.*, **260**, 19.
FEITKNECHT, W., AND MARTI, W. (1945), *Helv. Chim. Acta*, **28**, 129.
FRONDEL, C. (1953), *Am. Mineral.*, **38**, 761.
FRONDEL, C., AND HEINRICH, W. (1942), *Am. Mineral.*, **27**, 48.
GARRIDO, J. (1951), *Ion*, **11**, 453.
HAHN, H., AND KLINGLER, W. (1949), *Zeits. Anorg. Chem.*, **260**, 97.
VERWEY, E. J. W., AND DEBOER, J. H. (1936), *Rec. Trav. Chim. Pays-Bas*, **55**, 531.
WADSLEY, A. D. (1954), to be published.

SECONDARY ALTERATION OF CHROMITE

E. DEN TEX, *The University of Melbourne, Victoria, Australia.*

Readers of Roswell Miller's (1953) paper on the Webster-Addie Ultramafic Ring and the secondary alteration of its chromite, may be interested in similar alteration phenomena found in serpentinites of the Belledonne Massif near Grenoble, S. E. France, and described by the present author in a Ph.D. thesis for the University of Leyden (Holland). As the results are contained in a publication of rather difficult access, they are here summarized as far as the study of chromites is concerned.

Scattered grains of chromite occur in the serpentinitized ultrabasic core of a funnel-shaped basic intrusion in the hercynian basement of the Western Alps (Belledonne Range). The grains are coated with a highly ferromagnetic, black, opaque material which is also seen to penetrate along fissures in the grains. A colorless chlorite usually surrounds the

mantles and sometimes fills in fissures that have been left open after the formation of the black mesh structure in the original chromite. Optically the chlorite was found to be extremely rich in the amesite molecule.

Fractional panning and subsequent treatment with Clerici solution and the permanent magnet provided concentrations of the ore fraction sufficient for x-ray powder determination. Diffraction line doublets of the spinellide pattern for δ -angles larger than $25\text{--}30^\circ$ indicated the presence of two distinctly sized spinel lattices. Their unit cell dimensions were calculated from the outstanding (440) diffraction lines. One of these shows a very restricted range from 8.395 to 8.397 Å and evidently represents practically pure magnetite. The other a ranges from 8.16 to 8.269 Å and is believed to indicate various isomorphous mixtures of the Fe''-Mg-Al-chromite series. The part played by the magnetite molecule is of no consequence in this structure as the ferromagnetism of the chromite, especially where not coated with magnetite, is extremely weak.

A quantitative chemical analysis of the ore fraction of a serpentinite was carried out by the Petrochemical Laboratory of the University of Leyden and gave weight percentages of the following oxides:

SiO₂ 5.68; Al₂O₃ 15.77; Cr₂O₃ 10.12; Fe₂O₃ 44.26; FeO 15.34; MgO 9.28; CaO 0.00; TiO₂ 0.00; Total 100.45

Equiv. Weights		At	Be	Al ₂ O ₃	Mt	Fe ₂ O ₃
Si	95	95				
Al	310	190	43	77		
Cr	133		133			
Fe'''	554				330	224
Fe''	213		48		165	
Mg	230	190	40			
Total	1535	475	264	77	495	224
			341		719	
Molecular norm in per cent		31		22		47
Modal comp. in vol. per cent		±25		±25		±50

At = amesite; Be = beresofite; Mt = magnetite.

In the accompanying table the equivalent weights have been calculated according to Niggli's method (multiplication of the weight percentages of the oxides by 1000 and division of the respective molecular

weights into the figures so obtained). All available silica has been used in the formation of amesite (At). All chrome and remaining magnesia have gone into a non-ferric chromite whose proportions of ferrous iron and alumina were determined by plotting the line $a = 8.269 \text{ \AA}$ on Simpson's four constituent diagram of the non-ferric chromites and finding its intersection with the line representing the given Mg:Cr ratio. A chrome-rich beresofite (Be) was thus found, but the excess alumina is probably contained in the structure making it roughly a 1:1 chromespinel. The remaining magnetite must have a similar quantity of excess $\gamma\text{-Fe}_2\text{O}_3$ as no trace of either hematite or corundum have been detected in the x -ray powder diagrams. Kordes (1935) claims that equal quantities of excess R_2O_3 can be admitted to the spinel-structure without appreciably affecting its unit cell dimension.

The overall excess of the R_2O_3 molecule seems to indicate a high degree of oxidation during the formation of the magnetite mantles which are found coating the chromite grains in the *Triassic* but not in the *Carboniferous* basal conglomerate. These considerations exclude the possibility of a deuteric origin of the solutions causing the magnetite, and probably also the serpentine to develop. The alteration of the chromite is definitely post-basic-rock-consolidation and must have occurred at comparatively shallow depth.

Altered chromite in a serpentinite containing bastite after diallage is pale brown translucent and its smaller unit cell dimension ($a = 8.228 \text{ \AA}$) suggests a higher Al:Cr ratio, of primary origin because the volume percentage of magnetite coating is roughly equal to that found on the chromite with $a = 8.269 \text{ \AA}$.

Unaltered chromite in a highly silicified ultrabasic boulder from the Carboniferous basal conglomerate shows no signs of corrosion and its brown color and very small unit cell dimension ($a = 8.16 \text{ \AA}$) indicate an even higher Al:Cr ratio of doubtlessly primary nature.

Therefore, if the formation of magnetite and amesite has at all resulted in a composition change of the chromite, the latter must have been relatively enriched in chrome by the abstraction of alumina, whilst the removal of both magnesia by the amesite and ferrous iron by the magnetite could explain the excess R_2O_3 as well as the possible increase in unit cell dimension of the remaining chromite.

REFERENCES

- MILLER, R., III (1953), *Am. Mineral.*, **38**, 1134-1147.
TEX, E. DEN (1950), *Leidsche Geol. Mededelingen*, **15**, 1-204.
KORDES, E. (1935), *Zeit. Krist.*, **91**, 193-228.

NOTE ON THE SIGNIFICANCE OF "TURBID" FELDSPARS

ROBERT L. FOLK, *The University of Texas, Austin, Texas.*

One commonly reads in most textbooks on the subject that the turbid, brownish appearance of many feldspars (especially orthoclase) when viewed in thin section is due to the presence of a kaolin-like mineral. If examined under high power, however, the objects responsible for the "turbidity" are manifestly not kaolin-like clay minerals, but on the contrary represent simply liquid-filled vacuoles, similar in nearly every respect to the liquid-filled vacuoles in the quartz of igneous rocks. The evidence for this is: (1) the "turbid" objects have a high relief with refractive index well below that of the feldspar; the relief, though not measurable, is sensibly the same as that of liquid inclusions in quartz. This definitely rules out kaolinite as a possibility because both of the indices of this mineral are above the indices of potash feldspar; the only possibility other than liquid is that they are allophane or some other clay mineral with a very low index. (2) The "turbid" objects appear brownish in transmitted light and milky in reflected light, exactly like the liquid-filled vacuoles in granitic quartz or in chalcedonic quartz (Folk and Weaver, 1952). This is probably due to some complex dispersion effect, as nearly every object of lower index appears brownish when immersed in a medium of higher index; because both kaolin and sericite possess indices higher than that of the feldspar, they do not give this brownish appearance. (3) The "turbid" objects are isotropic, whereas kaolinized feldspars show a pinpoint birefringence in shades of gray to black, and sericitized (or illitized?) feldspars normally show white to yellowish birefringence. (4) The "turbid" objects have an irregular shape, with rounded protuberances; they frequently are somewhat elongated parallel with the crystal directions in the host feldspar. Other than the rather consistent elongation, their shape corresponds closely with the shape of known liquid-filled vacuoles in granitic quartz. (5) The "turbid" objects rarely contain a spherical, movable gas bubble.

To summarize, the brownish-appearing objects of high negative relief responsible for the turbidity of feldspars are liquid-filled vacuoles; both kaolin and sericite, on the other hand, have only moderate relief with indices higher than the potash feldspars, hence give no brownish cast and are anisotropic.

The significance of turbid feldspars is not clear. Under the assumption that the brownish "turbidity" was caused by a kaolin-like mineral, the phenomenon was easily explainable as a stage in the alteration of the feldspar either because of hydrothermal attack or weathering. If, on the contrary, the turbidity is caused simply by bubbles of water, a different

implication is thrown on the subject. Examination of several hundred thin sections in the teaching collections both at The Pennsylvania State College and The University of Texas has revealed the following tendencies: (1) feldspars of acid plutonic rocks and pegmatites are usually richly clouded with vacuoles which occur throughout most of the feldspar grain in a dense, pervading swarm; (2) feldspars of basic plutonic rocks and of both acid and basic extrusive rocks tend to have few vacuoles and the vacuoles that are present do not form dense pervading clouds but instead tend to be strung out along cleavages, fractures or certain crystallographic directions; (3) feldspars in weathered igneous rocks and in sediments, which are dull, whitish and soft in hand specimen, may either have legitimate clay-mineral alteration (shreds of clay with higher index than host feldspar) or else may be pervaded by the same dense swarms of vacuoles. That these turbidity-producing vacuoles do form in part by weathering is shown by specimens of the Upper Cambrian Gatesburg Formation of Pennsylvania; fresh specimens contain detrital and authigenic feldspars that are perfectly clear and free of bubbles, but in weathered float specimens both detrital and authigenic feldspars are thickly crowded with brownish-appearing bubbles.

Thus the following conclusions may be in order: (1) Some of the vacuoles may be primary to deuteric, trapped during crystallization from a magma or by attendant hydrothermal activity. Crystallization in a more hydrous environment (as in granites and pegmatites) favors entrapment of considerable water in the feldspars, therefore the feldspars in these rocks are usually "turbid" because they are richly clouded with vacuoles; feldspars crystallizing from a less hydrous magma (as in extrusive rocks) trap less water and are generally clearer. (2) Some of the vacuoles form on weathering, by a yet unknown mechanism (see Frederickson, 1953).

REFERENCES

- FREDERICKSON, A. F. (1951), Mechanism of weathering: *Bull. Geol. Soc. Am.*, **62**, 221-232.
FOLK, ROBERT L., AND WEAVER CHARLES EDWARD (1952), A study of the texture and composition of chert: *Am. Jour. Sci.*, **250**, 498-510.

SPOT GRINDING, A TECHNIQUE FOR FINISHING ROCK THIN SECTIONS

RONALD WILLDEN AND DAVID C. ARNOLD

*U. S. Geological Survey, Menlo Park, California, Phillips Petroleum
Co., Salt Lake City, Utah*

While preparing thin sections for petrographic study in the Mineralogy Department of the University of Utah, the authors encountered some difficulty in the preparation of sections in which the hardnesses of

the component minerals varied widely. In an attempt to overcome the problem, the technique of "spot grinding" was evolved.

The conventional procedure for grinding a thin section at the University of Utah involves cutting a thin slice from the specimen with a diamond saw and grinding it on two cast iron laps using dry — 240 mesh silicon carbide for coarse grinding and suspensions of — 600 and — 900 mesh silicon carbide in water for final grinding. Sections with a tendency to grind away on the fine lap were formerly finished on a heavy glass plate using a water suspension of — 2400 mesh aluminum oxide. Finishing the troublesome sections on glass plates worked satisfactorily in most cases but required considerable time and care to avoid losing the edges of the section. The technique described below was developed to supplant the use of a glass plate for final grinding.

The original apparatus consisted of an ordinary electric erasing machine fitted with disks of carborundum polishing paper. The disks were cut from Norton abrasive paper, grades 1 and 0, and cemented to solid head steel thumb tacks pressed in the ends of wooden dowels that could be inserted in the eraser holder of the machine. Disks of various sizes were tested and it was found that those about the same size as the thumb tacks gave the best results. Larger disks were useful on some sections, but they buckled and tore if much pressure was applied to the edge of the disk.

The thin sections were finished by grinding the "high spots" with the apparatus described above, thus the name "spot grinding." Two sheets of polaroid were used to check the thickness of the sections during grinding. One sheet was mounted on the underside of a glass plate, which served as the working surface and was illuminated from below, and the other was suspended over the grinding apparatus.

The technique was first used to finish a section of chlorite schist cut by several quartz veinlets. Grinding this type of rock by the conventional procedure resulted in most of the chloritic material being lost before the quartz veinlets reached the required thickness. By spot grinding it was possible to grind the quartz veinlets to 0.02 mm. without losing the chloritic material.

Spot grinding worked very well on most of the sections, but occasionally the generation of excess heat by the grinding disks resulted in partial melting of the canada balsam used as a cementing material. When melting occurred the portion of the slide where the balsam melted was lost. This difficulty was overcome by using a thermoplastic cementing material with a higher melting point than canada balsam, and by using a wet grinding compound on the thumb tacks instead of the paper polishing disks. The compound, a thick suspension of — 600 mesh silicon carbide in water, was applied to the section and grinding action was supplied by the thumbtack in the erasing machine. The wet grinding compound

smearing the section and the thickness could no longer be checked with the polaroid sheets as grinding progressed, but this was not a serious objection as an experienced thin section technician can check the thickness of a section by its appearance.

Spot grinding has several advantages over conventional methods of finishing thin sections. About two-thirds less time is needed to finish sections with this technique than by grinding on a glass plate. Spot grinding may be applied to any sections in which the hardness varies greatly, such as sections cut across the contact between altered and unaltered rocks. With this technique large sections of rocks, virtually impossible to finish otherwise, may be prepared. Spot grinding has been used to finish large thin sections for use as lantern slides, which are very difficult to grind to uniform standard thickness unless the grinding laps are absolutely flat, but with this technique high spots may be readily removed.

By action of the Council of The Mineralogical Society of America, Dr. Edward H. Kraus, Professor Emeritus of Crystallography and Mineralogy, and Dean Emeritus of the College of Literature, Science and the Arts of the University of Michigan, was chosen Honorary President of The Mineralogical Society of America, succeeding the late Professor Charles Palache. Dr. Kraus served as the first President of the Society (1920) and was the recipient of the Roebling Medal in February 1945.

Dr. Robert Charles Wallace, former Principal of Queen's University, died January 29-1955, at his home in Kingston, Ontario. He was 73 years old. Dr. Wallace had been Executive Director of the Arctic Institute in Montreal since his resignation as Principal of Queen's in 1951. Prior to accepting the call to Queen's University in 1936 he was Lecturer in geology and mineralogy at the University of Manitoba and President of the University of Alberta.

The Society for Experimental Stress Analysis will hold its 1955 Spring Meeting April 27, 28, and 29 at the Hotel Statler, Los Angeles, California. For further information regarding this meeting write Dr. W. M. Murray, Secretary-Treasurer, P.O. Box 168, Central Square Station, Cambridge 39, Mass.

The Society of Exploration Geophysicists will hold its tenth annual Gulf Coast Meeting at the Plaza Hotel, May 19 and 20, 1955, in San Antonio, Texas.

GRADUATE FELLOWSHIP IN MINERALOGY

The Ohio State University announces a graduate fellowship for 1955-1956 to encourage research on phase-equilibrium relationships of silicate minerals. The stipend is \$1500 for 9 months, with no teaching duties required. Further information can be obtained from Professor W. R. Foster, Department of Mineralogy, The Ohio State University, Columbus 10, Ohio.

Correction

This is to record the misspelling of the mineralogical name "rabbittite" three times on page 1037 of the November-December 1954 issue of *The American Mineralogist*.

BOOK REVIEWS

RÖNTGENKARTEI ZUR BESTIMMUNG VON TON- UND SEDIMENTMINERALEN, by HEINZ URBAN. Published by Verlag Gustav Feller-Nottuln, Kettwig/Ruhr, Germany. Pp. 37+iv+25 plates. (Publication No. 5 of *Opuscula Mineralogica et Geologica*, edited by Erwin Nickel, Münster.)

The theme of this work is the identification of clays and other fine grained minerals found in sediments by means of x-ray powder diagrams. The author is aware that other books on this subject have appeared in recent years, but he aims at remedying two deficiencies, namely (1) the lack of determinative tables and diagrams in the German language, and (2) the absence of a concise account suitable for the general worker rather than the specialist. The book covers about 60 minerals and besides the clay minerals it considers the more common oxides, hydroxides, carbonates and silicates found in fine grained sediments. Short notes on each mineral supplement the tables and diagrams and make the reader aware of some of the difficulties of the subject and of special auxiliary techniques. The data tables are printed on the backs of the corresponding diagrams which are collected together at the end of the book; the diagrams can be cut out to a standard size and arranged in the manner of a card index. This part of the book is clear and well written and fulfills the objective of a simple treatment for the general worker. The reviewer considers that a mentally-active worker would soon become aware of the complexities of the subject and would then turn to one or other of the more specialized texts which are available.

The introductory section of the book dealing with the determination of d -values from film measurements is very poorly written; in places it is both misleading and incorrect. The correction of film distances, A , in the Straumanis method is given as follows:

$$A \text{ (corrected)} = A \text{ (measured)} + K_2$$

and

$$K_2 = (P - U)/P$$

where P and U are the ideal and measured lengths corresponding to a 2θ range of 180° . Thus K_2 is a dimensionless ratio and incompatible with the first equation. The text says that K_2 must be expressed as a *percentage* of A (measured), which also is incorrect. The correct statement is: $K_2 = [(P-U)/U]A$ (measured). In any case, this way of stating the correction is needlessly cumbersome, since all that is required is

$$A \text{ (corrected)} = A \text{ (measured)} \times P/U.$$

The description of the correction for specimen thickness is equally bad.

Turning next to the important question of wavelengths and units, we look for clear guidance on the use of kX and Å units. The account given is incorrect and confusing. The author distinguishes between the Å unit and a metrical unit, 10^{-8} cm.; the relation between them is given as $1 \text{ Å} = 1.00202$ metrical Å units. The metrical Å unit (we are told) is designated KX in American literature. An adjacent table of wavelengths gives for Cu(K_α) the value of 1.539 Å units (not Å units). The author may like to know that $1 \text{ Å} = 10^{-8}$ cm., and that the X-unit, first used by Siegbahn about 1923, is defined as $1/3029.04$ of the effective (200) spacing of calcite at 18°C. , so that 1 kX unit is approximately 1 Å or 10^{-8} cm. To convert values in kX to values in Å units, the kX value is multiplied by 1.00202. Therefore $1 \text{ Å} = (1/1.00202) \text{ kX units}$: the kX unit is larger than the Å unit, so that any distance expressed in kX units has a smaller numerical value than the same distance expressed in Å units.

The reviewer considers that the first section of this book should be re-written.

G. W. BRINDLEY,
Pennsylvania State University, State College, Pa.

GEOLOGIE DER SCHWEIZERALPEN, by J. CADISCH AND E. NIGGLI. Wepf & Co., Basel, 1953. 44.- SFr.

Although, *sensu latu*, the term geology includes petrology as well, the new edition of Cadisch's *Geology of the Swiss Alps* could be called: *Geology and petrology of the Swiss Alps* since the co-author, Prof. E. Niggli from the University of Leiden is a petrologist. Dr. J. Cadisch is professor of geology at the University of Bern. Whereas the first edition (1934) was basically a textbook, the new edition is more a handbook. The individual sections are written in such a way that they can be read and used separately and special care has been taken to refer to the important literature. For the following reasons the excellent section on petrology and mineralogy is of interest to the American mineralogist and petrologist. The summary on the petrology of igneous rocks (p. 21–80) and of metamorphic rocks (p. 80–119) of the Alps is the best, the most complete and up to date outline on this subject. It is not only a perfect review of what has been done so far, but also a good program for future research. The same is true for the section on sedimentary rocks (p. 120–188) and the rest of the book.

The whole volume (including 491 pages, with 59 figures) is very well illustrated and has remarkably few printing errors. It contains three sections: I. Introduction and generalities. (p. 1–20). II. The “building materials” of the Swiss Alps (rocks, stratigraphy and tectonics). III. The landscapes (tectonics and morphology) of the Swiss Alps (p. 290–444).

The section by Prof. E. Niggli includes outlines on the petrochemistry of igneous and metamorphic rocks of the Swiss Alps (by tectonic and/or regional units, partly as syntheses which, in this book, are published for the first time). Included is also a brief summary on the famous fissure minerals (Kluftmineralien which are thoroughly described in the new book by Prof. Parker, printed by the same editors). It represents an almost complete coverage of the newer and, to a certain extent, also of the older literature. It is the most up to date guide to the literature and the problems of alpine petrology and mineralogy (and geology!), and should, therefore, be highly recommended to the American worker interested in this subject.

There is one thing which is almost completely left out and which especially the economic geologist and mineralogist will miss: a brief summary on alpine ore deposits. Ore deposits connected with ophiolites are practically the only ones mentioned. Although almost all ore deposits of the Swiss Alps are not commercially important, they are, genetically and mineralogically, extremely interesting. Moreover, they play a rather important role in the discussion on the genesis of many gneisses and granites (palingenesis versus juvenile). Schneiderhöhn, in a recent publication, classifies most alpine ore deposits as being re-worked paleozoic or even older deposits, whereas P. Niggli (in his unpublished guide for a field trip to Austria) presented many strong arguments for a young, alpine age of most alpine ore deposits. It is certain that a careful re-study of the very numerous though small ore deposits could be used as one of the keys to many unsolved problems on alpine petrogenesis.

In the section on petrology and mineralogy of Swiss alpine igneous rocks there are two things which must impress the reader. *Firstly*: there is probably no other mountain belt in the world where the classical tools of the petrologist have been applied so thoroughly and carefully: the hammer and the map, the microscope and the chemical analysis. *Secondly*: it is remarkable, too, that, since Professor Niggli set this tradition in the twenties, many workers have, again and again, correlated these observations to the newest data of physical-chemistry.

On the other hand, it becomes obvious that other methods should be applied as well—many of which have been developed only recently and afford partly a close team work between different universities, the industry and the state (because the equipment needed is very expensive).

Some of these newer methods are: spectroscopic analysis of rocks and minerals (for trace element geology), mass spectroscopy (for isotope geology), age determinations, radioactivity measurements, assaying of ore deposits, drilling (for solving problems of tectonics, stratigraphy and economic geology), field-emission microscopy, electron diffraction, and reflection-electron microscopy (for studies of solid surfaces); differential thermal analyses, etc. It is obvious throughout the book (although hardly ever mentioned) that many problems of alpine geology will never be solved without the application of one or more of these modern methods. To mention just two examples: (1) A relatively small number of age determinations could solve quite a number of very vital problems, such as the age of the volcanic rocks in the Taveyannaz-sandstone, the age of the intrusive members of many nappes, of the Casanna-schists, etc. (2) Whereas the geochemistry of the major elements of Swiss rocks, minerals and soils is relatively well known, the trace element geology is far behind. Yet, it is well known that many rocks and stratigraphic units can only be differentiated and/or genetically understood with the help of trace element composition.

At any rate, there is no better reference book and guide to alpine petrology and mineralogy than the new, completely revised edition of "Geologie der Schweizeralpen."

G. C. AMSTUTZ,

Cerro de Pasco Corporation, La Oroya, Peru

A FIELD GUIDE TO ROCKS AND MINERALS, by FREDERICK H. POUGH, xv+333 pp.
Houghton Mifflin Company, Boston, Massachusetts, 1953. Price \$3.75.

This book is a most useful companion to the previously published members of the Peterson Field Guide Series. It is divided into two parts: I. An Introduction to the Study of Rocks and Minerals, which contains chapters on Your Mineral Collection, Rocks and Minerals and Where to Find Them, Physical Properties of Minerals, and Tests, Techniques, and Tips. II. Mineral Descriptions. A useful glossary, a selected bibliography, and an index are appended.

There are 34 figures, 254 photographs (72 in color), 228 crystal drawings, and 2 end-paper diagrams. The photographs of the minerals, especially those in color, are the best this reviewer has seen. The minerals are pictured against an enhancing background of variously colored, uniformly ribbed corduroy which provides a scale for size. Crystal drawings, usually showing two different habits, accompany each of the photographs. The photographs of the rocks are not as well done; in particular those appearing on Plate 1 do not seem to be in true color, and no scale has been provided as for the minerals.

A great amount of useful knowledge has been packed into this small (19×12 cm.) book. It is primarily intended to serve as a practical field guide for the amateur mineralogist-collector, but it will be appreciated by the professional mineralogists who lack perfect memories. There are presented many interesting and little-known facts about minerals; there is more data on luminescence than is usually found in other sources. Several new diagnostic tests are presented, especially those utilizing the color of fluorescence after ignition. The inclusion of Herman-Mauguin space-group symbols, while not essential in an elementary work, none the less consumes very little space. The minerals described (nearly 250) have been wisely selected and include as many, or more than the average collector is likely to find.

Since there are no determinative tables, the book must be read through completely to be of most use. With such a readable account as this, however, that can hardly be considered as a chore. In short the amateur or professional mineralogist will find the book a convenient and valuable guide.

RICHARD C. ERD,

U. S. Geological Survey, Washington 25, D. C.

GEOGRAPHICAL ESSAYS, by WILLIAM MORRIS DAVIS. Dover Publications, Inc., New York, 1954. vi+777 pages. Price \$5.50.

Between 1889 and 1906, William Morris Davis published a series of essays, written in his very readable style, in several different domestic and foreign journals. These essays dealt with various aspects of geography—its place in both primary and secondary schools and in universities; the teaching of geography, methods and the use of field work and models; geography as a study of land forms and how they originated; the history of rivers; glacial sculpture of mountains and many others. Realizing the value of these writings of his teacher and colleague, Douglas Johnson gathered together the ones that he considered most representative, grouped them for content, edited them to a certain extent (with W.M.D.'s approval), and published them in 1909. The volume was well received and in the past 45 years, it has stood the test of time and proved that the subject matter is sound, that the author was a master at presenting it and that the editor recognized both of these things.

The present volume is an unabridged republication of the original. It is divided into two parts: Part I comprises 12 Educational Essays containing some articles on the techniques of teaching geography and others consisting of material for use by teachers of geography. Part II—Physiographic Essays, reproduces the classic essays on The Geographic Cycle (The Cycle of Erosion), Complications of the Geographic Cycle, the Geographic Cycle in an Arid Climate, The Plains of Marine and Sub-Aerial Denudation, The Peneplain, and Base-Level, Grade, and Peneplain, in which Davis laid the theoretical foundations of modern Geomorphology (which he preferred to call Physiography), and established the nomenclature that, with very minor changes and additions, is in use to-day. The other eight essays of Part II are regional applications of the principles laid down in the first six. The original journal references are given with the titles in the Table of Contents.

It is appropriate that this series of classic essays should be republished when geomorphology is being established as a full-fledged branch of geology and is aiding in the solution of such diverse problems as the ages of the Tertiary and Quaternary basalts in Iceland, the origin and the uranium content of the land phosphate of Florida, and the relation between ground-water circulation and the depth of secondary enrichment of copper deposits in southern Arizona.

It is unfortunate that such an important book, even though it is a reprint, should be on inferior paper, be poorly bound and have the author's name spelled "Davies" on the shelf back.

EARL INGERSON,
U. S. Geological Survey, Washington, D. C.

PROBLEMS OF CLAY AND LATERITE GENESIS. A Symposium of *A.I.M.E.* (1951) x+244 pp. 63 text figs., 6×9, Cloth. *American Institute of Mining and Metallurgical Engineers*, New York City (1952), \$6.00 (\$4.20 to *A.I.M.E.* Members).

This book is a collection of papers presented at the symposium.

"The genetic significance of mineralogy," by A. F. Frederickson, is an attempt at a graphical representation of the origin of the four groups of minerals that make up clay and laterite deposits: (a) aluminum hydroxide minerals, (b) iron oxide and hydroxide minerals, (c) titanium oxide minerals, and (d) the clay minerals. These graphs are based on laboratory data and description of the field occurrences of these minerals.

"Origin of the Arkansas bauxite deposits," by Mackenzie Gordon, Jr., and J. I. Tracey, Jr. This is a well organized, nicely illustrated, and interestingly written account of the genesis of these deposits. An excellent description is given of the stratigraphy of the four types of deposits. The figures and photomicrographs are well chosen to illustrate the data on which the origin of the deposits is based.

"Examples of bauxite deposits illustrating variations in origin," by E. C. Harder, presents a critical survey of the derivation of bauxite from various kinds of rocks. Harder discusses the derivation of bauxites from: (a) rocks rich in alkali-aluminum silicates, (b) limestone, (c) sedimentary clays, (d) intermediate and basic igneous rocks, (e) rocks of moderate alumina content. This section contains a handy summary description of noteworthy bauxite deposits in various parts of the world. A vertical section showing the lithologic relationship is given for each type of bauxite genesis.

"Investigations on cold-precipitated hydrated ferric oxide and its origin in clays," is treated by R. C. Mackenzie. This substance is of widespread occurrence in soil clays. The method of preparation of this substance and characteristic differential thermal analysis curves and x-ray data are given.

"Studies in the system alumina-silica-water," by Rustum Roy and E. F. Osborn, presents a summary of their data on this system as derived from hydrothermal synthesis studies. Univariant equilibrium curves for the system are given along with the composition triangles containing the stable phase assemblages.

"Mineralogy and origin of the Mercer fireclay of north-central Pennsylvania," by R. C. Bolger and J. H. Weitz, describes the occurrence of the diasporite and boehmite-rich members of the Mercer group. Particular emphasis is placed on the genesis of the "high-alumina" fireclays. A paragenetic chart is presented for the 10 minerals of the Mercer fireclay.

"The structure of hydrous aluminum oxides and hydroxides," by W. O. Milligan and J. L. McAtee, summarizes the status of the x-ray data on gibbsite, bayerite, boehmite, and diasporite and discusses the alumina that is amorphous to x-rays.

Professor Ernest A. Hauser has written two chapters for this volume. The first, entitled "Genesis of clay minerals," presents a theory of origin of clay minerals based on concepts of the physical chemistry of colloidal materials. Professor Hauser is not satisfied with the present concept of the origin of clays as residual materials or as transported clays. He believes that colloidal phenomena are more important than most geologists and mineralogists will admit. The second chapter concerns the Kisameet Bay clay deposit of British Columbia. The clay material is very fine grained, and its mineralogy has not been completely characterized.

Professor Georges Millot of the University of Nancy, France, has written a very interesting chapter, "Prospecting for useful clays in relation with their conditions of genesis," explaining the observations he has made in this field and his method of interpretation.

"Observations on the origin of Missouri high-alumina clays," is written by W. D. Keller. On the basis of new geologic evidence—the discovery of a Pennsylvanian rock cover lying undisturbed over high-alumina clay—and on physico-chemical considerations, Professor Keller has proposed a new theory of origin for the diasporite and boehmite-rich clays. Diasporite and boehmite were formed under reducing conditions possibly at or under the ground-water table. They "are not laterites in the sense that gibbsite is, which forms in a strong oxidizing leaching environment."

In "New clay mineral evidence concerning the diagenesis of some Missouri fireclays," by John F. Burst, x-ray powder diffraction studies of a Missouri plastic fireclay show that the major clay mineral, although a member of the kaolinite group, is not kaolinite. The data are best reconciled with an alternate stacking of the lower and upper silica sheets, originally proposed by Gruner in his study of dickite. Burst suggests that this major clay mineral is a new mineral.

"Interrelationships of structure and genesis in the kaolinite group," was contributed by Thomas F. Bates. This is a discussion of some of the available data bearing on the genesis of kaolinite, endellite, halloysite, and allophane. A diagram showing the stability of endellite and halloysite as a function of vapor pressure and as a function of the temperature is used in these interpretations.

"The genesis and morphology of the alumina-rich laterite clays," by G. Donald Sherman, is a discussion of the weathering of the basaltic rocks of the Hawaiian Islands under several different sets of climatic conditions with the production of lateritic deposits. Rainfall is considered to be a dominant factor in the laterization process.

"Occurrence and exploration of Georgia's kaolin deposits," by T. L. Kesler, is a description of the geology of the clay deposits and the methods of prospecting. The need for a new theory of origin of the kaolinite deposits is presented.

The concluding chapter is by Ralph E. Grim and is entitled "Recent advances in clay mineral technology." This is a well integrated summary of recent work on clay minerals as applied to problems in ceramics, the oil industry, soil mechanics, bonding clays, and the alteration zones around ore deposits.

A record of the discussion that followed the presentation of these papers is made a part of the book.

The reviewer strongly recommends this book to those working with clays and to teachers in the earth sciences.

GEORGE T. FAUST,
U. S. Geological Survey, Washington 25, D. C.

ZUR GEOLOGIE, PETROGRAPHIE UND MINERALOGIE DES WESTHARZES.
Vereinigung der Freunde der Mineralogie und Geologie; Rossdorf bei Darmstadt. 55 pages, 1954.

This paper-bound pamphlet, a collection of 11 papers on the geology, petrography and mineralogy of the western Harz Mountains, Germany, each paper by a different author, was issued in connection with the annual meeting of the Society of the Friends of Mineralogy and Geology of Rossdorf near Darmstadt at Clausthal-Zellerfeld in the Harz Mountains in 1954. Among the features described are the rocks of the Harzburg gabbro massif (A. Werner), stratigraphy and tectonics (W. Schriel), tectonic setting and fold patterns of the upper Harz (W. Schwan), the Rotliegende in the southern Harz (Th. Kruckow), magmatic rocks (W. E. Tröger), a cross section of the west Harz (W. Simon), the Rammelsberg ore deposit (E. Kraume), the lead-zinc veins of the upper Harz (E. Hüttenhain), the veins of St. Andreasberg (A. Wilke), the iron ore deposits of the upper Harz (Fr. Buschendorf), and a brief history of upper Harz mining and mining towns (A. Riechers). There also are included a short introductory statement (The Harz—a geological treasure), a tribute to Friedrich Adolph Roemer (1809–1869)—from collector to investigator, and a selected bibliography of geologic literature on the Harz.

E. WM. HEINRICH,
University of Michigan, Ann Arbor, Mich.

URAN. DIE METALLISCHEN ROHSTOFFE, 10. Heft, by E. KOHL, edited by Ferdinand Friedensburg. 234 pages, 23 figures, 35 tables. 1954. Ferdinand Enke Verlag, Hasenbergsteige 3 (14a), Stuttgart-W., Germany. Paper cover DM 26.00, linen cover DM 29.00.

This is volume ten, on Uranium, of the well known encyclopedic series on metallic raw materials. The book consists of two parts: Part I—General, and Part II—Deposits by individual countries. In the first section the various chapters are on properties, occurrence and origin—minerals, rocks, mineral and ore deposits (primary, secondary, radioactive waters and gases, helium occurrence), prospecting and mining, preparation and uses, history, market conditions and value, supply, and production. In Part II deposits in 62 countries are described.

The description of the minerals that contain uranium is poor—consisting of six brief

tables which are incomplete and which list varieties and some inadequately known members. Other minerals in which uranium may be a minor but significant constituent, such as apatite or zircon, are not mentioned. The discussion of the various types of deposits is also very brief. The most valuable section of the book is Part II in which deposits are described individually, by countries and each country is followed by a list of references. Most of the descriptions are relatively up to date.

Doubtless this book, because it is a modern summary of known deposits available, will receive widespread reference use among geologists and mining engineers.

E. WM. HEINRICH,

University of Michigan, Ann Arbor, Mich.

GEOLOGIE UND PETROGRAPHIE DER ERGUSSGESTEINE IM VERRUCANO DES GLARNER FREIBERGES, by G. CHRISTIAN AMSTUTZ. Vulkaninstitut Inmanuel Friedlaender, Min.-Petro. Inst. Eidg. Tech. Hochschule Zürich. Nr. 5. 149 pp. 12 plates. Zürich (1954).

This is a beautifully prepared study of the volcanic rocks of the Glarner Freiberg, Switzerland—mainly spilites, keratophyres, rhyolites and acid tuffs. Most of the monograph deals with the petrography of these rocks, but other chapters consider their occurrence, chemistry, classification and radioactivity. The writer concludes that primary spilite-keratophyre provinces exist, but on the origin of spilites he straddles—saying his ideas lie between those who regard spilites as strictly magmatic and those who believe them strictly metasomatic.

E. WM. HEINRICH,

University of Michigan, Ann Arbor, Mich.

STRUCTURE REPORTS FOR 1950. Vol. 13. General Editor A. J. C. WILSON; Section Editors: N. C. BAENZIGER (Metals), J. M. BIJVOET (Inorganic Compounds), J. MONTEATH ROBERTSON (Organic Compounds). Published for the *International Union of Crystallography*. N.V.A. Oosthoek's Uitgevers Mij., Utrecht, Holland. viii+644 pp. (1954). Price 80.- Dutch florins, postpaid. Alternative: Polycrystal Book Service, 84 Livingston St., Brooklyn 1, N. Y. \$21.50.

The great importance and value of these *Structure Reports* have been fully established by the earlier volumes 10, 11 and 12, and no additional comments are necessary. It is gratifying that the editors and co-workers are able to carry on with this undertaking which is so extremely useful to all workers in the many fields where crystal structure is of importance.

LEWIS S. RAMSDELL,

University of Michigan, Ann Arbor, Mich.

NEW MINERAL NAMES

Kamiokalite

K. SAKURAI, H. NAGASHIMA AND E. SORITA, Kamiokalite, a new zinc copper phosphate mineral from Kamioka Mine, Japan. *Syumi-no-Tigaku (Amateur Geologist)*, 5, 170-175 (1952).

The mineral occurs associated with native silver, malachite, or hemimorphite, in the fissures or cavities of the decomposed skarn of the Urusiyama deposit of the Kamioka Mine, Gifu Prefecture, Japan. It is prussian blue in color, and the streak is pale blue. Transparent or translucent with a strong glassy lustre; cleavages are not developed. Fracture is conchoidal and hardness is 3-3.5. Octahedral crystals may attain a size of 2 mm., but usually they are less than 1 mm. in length. It occurs also as a thin film on the skarn. Measurements of a beautiful crystal, 1.5 mm. in size, show the mineral to be monoclinic, with $e\{011\}$, $m\{110\}$, and $i\{\bar{1}11\}$. Axial ratio: $a:b:c=0.734:1:0.966$, $\beta=76^{\circ}07'$. An analysis by Sorita on pure material, 0.2 gr. in weight, gave PbO nil, CuO 30.52, ZnO 32.44, (Fe,Al)₂O₃ 0.31, P₂O₅ 17.96, As₂O₅ nil, H₂O(+) 17.26, H₂O(-) 1.62. Insol. residue 0.72; total 100.83. From this the chemical formula obtained was $3\text{CuO} \cdot 3\text{ZnO} \cdot \text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$. Optical properties are: $\alpha=1.630$, $\beta=1.645$, $\gamma=1.683 (\pm 0.001)$, $\gamma-\alpha=0.053$. Weak pleochroism from blue to pale blue. 2V calc. = (+)65.5°.

DISCUSSION: The present mineral has mineralogical properties, intermediate between those of arakawaite, a zinc copper phosphate mineral described by Wakabayashi and Komada, and those of veszelyite, a zinc copper arseno-phosphate, described by Schrauf in 1874. The arakawaite has a chemical formula of $6(\text{Cu,Zn})\text{O} \cdot \text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$, and is monoclinic, while veszelyite has a formula of $6(\text{Zu,Zn})\text{O} \cdot (\text{As,P})_2\text{O}_6 \cdot 7\text{H}_2\text{O}$ and is referred to as triclinic (pseudo monoclinic). It is plausible that these two minerals form a solid solution series, and the present mineral may be a variety rich in zinc. The name is for the Kamioka Mine.

P.S. In his letter of Sept. 15, 1954, Sakurai informed the reviewer that a *x*-ray diagram of kamiokalite obtained with a North American Philips *x*-ray spectrometer agrees closely with that of arakawaite or veszelyite. Therefore he is of the opinion that these three minerals have similar structures, and that the kamiokalite should be described as a variety of veszelyite, rich in zinc. An analysis of the crystal structure of kamiokalite is now in progress.

KENZO YAGI

Belovite

L. S. BORODIN AND M. E. KAZAKOVA, Belovite—a new mineral from an alkaline pegmatite. *Doklady Akad. Nauk. S.S.S.R.*, 96, 613-616 (1954).

Analysis (by M.E.K.) gave rare earth oxides 24.00, SrO 33.60, BaO 0.96, CaO 5.23, Na₂O 3.60, K₂O 0.20, MgO 0.16, Fe₂O₃ 0.60, P₂O₅ 28.88, SiO₂ 0.20, SO₃ 1.12, H₂O 0.89; sum 99.44%. The rare earths include Ce₂O₃ 11.25%. *X*-ray determinations (*x*-ray spectroscopy?) by L. A. Voronov gave the ratios Ce:La:Nd:Pr = 1:0.6:0.5:0.2, which, if Ce₂O₃ is taken as 11.25, give La₂O₃ 6.75, Nd₂O₃ 5.62, Pr₂O₃ 2.25%. (Note: These add to 25.87 compared to 24.00% reported in the analysis. M.F.). The analysis conforms to the apatite group formula, A₁₀(PO₄)₆X₂, giving (Sr_{4.6}Ce, etc._{2.4}Na_{1.6}Ca_{1.3}Ba_{0.1})(P_{5.8}SO_{0.2})(O_{24.6}OH_{1.4}). (No mention is made whether F or Cl were tested for. M.F.). Belovite is therefore the strontium analogue of hydroxylapatite, but also contains rare earths and sodium. It is easily soluble in dilute nitric and hydrochloric acids.

X-ray study by N. N. Sludsko and N. I. Organov show belovite to be hexagonal with

$a=9.62 \text{ \AA}$, $c=7.12 \text{ \AA}$, $c/a=0.74$. The powder pattern is given; the strongest lines are 2.87 (10), 1.998 (8), and 1.900 (8).

Belovite occurs in prismatic crystals up to 2 cm. with (10 $\bar{1}$ 0) and (0001) prominent. Cleavage prismatic and pinacoidal, imperfect, usually noted in thin section. Fracture irregular. Color honey-yellow, luster vitreous, greasy on fracture. The mineral is brittle, $H=5$, $G=4.19$. Optically uniaxial, neg., $\omega=1.660$, $\epsilon=1.640$, birefringence=0.020.

The mineral occurs in a pegmatite in nepheline syenite, locality not stated (Kola Peninsula? M.F.). The principal minerals of the pegmatite are eudialyte, ussingite, and aegirine; minor constituents are sodalite, natrolite, microcline, murmanite, erikite, schizolite, neptunite, steenstrupine, and nepheline. Eudialyte and aegirine are localized in the border zone of the pegmatite; ussingite, natrolite, and belovite occur in the central part. Belovite occurs in ussingite, which was formed by late stage replacement of microcline.

The name is for N. V. Belov, Russian mineralogist and crystallographer.

MICHAEL FLEISCHER

Evenkite

A. V. SKROPYSHEV, A paraffin from a polymetallic vein. *Doklady Akad. Nauk S.S.S.R.* **88**, 717-719 (1953); from *Mineralog. Abs.*, **12**, 305 (1954).

The name evenkite is given to a crystalline hydrocarbon found in geodes lined with chalcedony and quartz in a vein cutting vesicular lava, Evenki region, Lower Tunguska River, Siberia. The vein contains pyrite, pyrrhotite, sphalerite, galena, chalcocopyrite, calcite, chalcedony, and quartz. The hydrocarbon is colorless or yellowish, wax-like, $G=0.873$, $H=1$, m.p. 49-51° C. It contains C 85.43, H 14.99%, corresponding to $C_{12}H_{12}$. It is soluble in ether. The crystals are biaxial positive, 2V small, $\alpha=\beta\leq 1.504$, $\gamma\approx 1.553$. The crystals show a good mica-like cleavage and polysynthetic twinning.

M. F.

Parasymplesite

TEI-ICHI ITO, HIDEO MINATO AND KIN'ICHI SAKURAI, Parasymplesite, a new mineral polymorphous with symplesite. *Proc. Japan Acad.*, **30**, 318-324 (1954).

Crystals from Kiura, Ohita, Japan, are about $3\times 1.5\times 1$ mm. in size. Goniometric measurements and Weissenberg photographs show them to be monoclinic, space group $C2/m$; the unit cell has $a\ 10.25$, $b\ 13.48$, $c\ 4.71 \text{ \AA}$, $\beta\ 103^\circ 50'$, and contains $2(Fe_3(AsO_4)_2\cdot 8H_2O)$; $a:b:c=0.760:1:0.350$. The type symplesite from Felsöbanya, Rumania, was found to be triclinic, in agreement with the work of Wolfe, *Am. Mineral.*, **25**, 801 (1940). The name parasymplesite is proposed for the monoclinic dimorph. Analysis gave As_2O_5 , 38.43; Fe_2O_3 , 0.81; FeO , 37.70; MgO and CaO , none; P_2O_5 , none; H_2O^- , 10.67; H_2O^+ , 12.70; sum 100.33% X -ray powder data are given; for the strongest lines are (in \AA): symplesite 6.785, 7.499, 8.971; parasymplesite 6.830, 7.063, 9.006, 7.499. Twenty forms were noted on parasymplesite crystals; prominent faces were $b\{010\}$, $w\{201\}$, $m\{110\}$, $E\{502\}$ and $t\{401\}$. Parasymplesite has a very perfect cleavage after $\{010\}$. Hardness=2, $D_{20}\ 3.07$ measured, 3.097 calculated. Optically negative (?) with large 2 V, $\alpha=1.628$, $\beta=1.660$, $\gamma=1.705$, $c\wedge Z\ 31^\circ 20'$. X =bluish green, Y =yellowish, Z =brownish yellow.

M. F.

Arsenosulvanite

A. G. BETEKHTIN, The new mineral arsenosulvanite. *Zapiski Vses. Mineral. Obshch. (Mem. soc. russe mineral)*, **70**, 161-164 (1941) (English summary).

V. I. MIKHEEV, The structure of arsenosulvanite, *Ibid.*, 165-184 (1941) (English summary).

These papers, not previously abstracted in this journal, describe a new mineral occurring in quartz-calcite veins cutting bituminous limestone in Mongolia. Analyses gave Cu 48.84, 46.65; S 33.14, 31.66; As 12.80, 11.67; V 4.16, 5.20; insol. 1.01, 3.82, sum 99.95, 99.00%. This corresponds to $\text{Cu}_3(\text{As}, \text{V})\text{S}_4$ with As:V about 2:1. Color bronze-yellow, $H. = 3\frac{1}{2}$, $G. = 4.01, 4.2$. Cubic, with $a = 5.257 \pm .003 \text{ \AA}$. Detailed data are given on the structure which is like that of sphalerite. Space group T_d^1 .

M. F.

Aldanite

M. M. BESPALOV, A find of a new member of the thorianite group. *Soviet Geol.* 1941, No. 6, pp. 105–107 (in Russian).

In this paper, not previously abstracted in this journal, three analyses are given of a cubic mineral, $a = 5.539 \pm .005 \text{ \AA}$ and $5.578 \pm .009 \text{ \AA}$ on 2 samples, found in placers in the Aldan River. The analyses show ThO_2 64.3, 69.3; UO_3 14.9, 20.4; PbO 11.2, 12.5%. Hardness = $6\frac{1}{2}$, $G. = 8.92$. The mineral is evidently a uranoan plumboan thorianite and the name aldanite is unnecessary.

M. F.

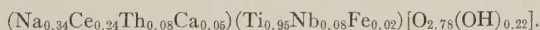
Irinite

L. S. BORODIN AND M. E. KAZAKOVA, Irinite—a new mineral of the perovskite group. *Doklady Akad. Nauk S.S.S.R.*, 97, 725–728 (1954) (in Russian).

Irinite occurs as cubic crystals with cube and octahedron faces and in fluorite-like penetration twins; the crystals are up to 1 cm. in size. The color is reddish-brown, brown, occasionally brownish-yellow. Streak brownish-yellow. Cleavage absent, fracture conchoidal. Luster greasy. In thin section isotropic, $n = 2.105$. Hardness = $5-5\frac{1}{2}$, $G. = 4.476$. Not attacked by HCl or HNO_3 , slowly decomposed by warm H_2SO_4 .

Irinite is metamict. It gives few x-ray lines when heated to 200° , more at 470° , and when heated at 650° it gives a pattern of the perovskite group with strongest lines at 2.71 (10), 1.919 (9), 1.569 (8), and 1.028 (6). From the powder data, the calculated edge for the smallest cell is $a_0 = 3.83 \text{ \AA}$. (should be 7.66 \AA ? M.F.).

Analysis (by M.E.K.) gave TiO_2 46.45, ThO_2 13.00, $(\text{Ce, etc.})_2\text{O}_3$ 24.00, $(\text{Nb, Ta})_2\text{O}_5$ 6.31, Fe_2O_3 0.88, CaO 1.83, Na_2O 6.41, H_2O^+ 1.22, HeO^- 0.03; sum 100.13%, corresponding to



A dehydration curve is given. Most of the water is lost between 400° and 650° .

The mineral occurs in nepheline syenite pegmatite, locality not stated (Kola Peninsula? M.F.), closely associated with aegirine and catapleite between crystals of the most abundant minerals, microcline and arfvedsonite. Other minerals present include nepheline, eucoelite, ilmenite, and astrophyllite.

The name is for Irin Dmitriev Borneman-Starynkevich, Russian mineralogist.

DISCUSSION: Irinite is a thorian variety of loparite, which is essentially $(\text{Na, Ce, Ca})(\text{Ti, Nb})\text{O}_3$, and the name is unnecessary.

M. F.

Peligotite (= Johannite)

V. G. MELKOV, Peligotite—a new mineral species. *Zapiski Vses. Mineral Obshch. (Mém. soc. russe minéral.)*, 71, 9–11 (1942).

In this paper, previously overlooked in this journal, the author describes a yellow-green uranium sulfate from the Taboshar deposit, North Tadzhikistan. The physical and optical

properties were recognized by him to be very close to those of johannite (gilpinite), but two chemical analyses gave the formula $\text{CuO} \cdot 2\text{UO}_3 \cdot 2\text{SO}_3 \cdot 3\text{H}_2\text{O} + 6\text{H}_2\text{O}$, different from that then accepted for johannite. The name is for Eugène-Melchior Peligot, who first prepared metallic uranium in 1841.

DISCUSSION: The formula now accepted for johannite is $\text{CuO} \cdot 2\text{UO}_3 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and the name peligotite should be relegated to the synonymy.

M. F.

NEW DATA

Bazzite (= scandian beryl?)

H. HUTTENLOCHER, TH. HÜGI AND W. NOWACKI, Röntgenographische und spektrographische Untersuchungen am Bazzit vom Val Strem (Kt. Graubünden, Schweiz). *Experientia* 10, No. 9, 366-367 (1954).

Spectrographic analysis showed bazzite to contain mainly (very strong) Be, Si, Al, Mg, Sc; (strong) Fe, Na, Ba; (medium) Ca, Sr. Also present (weak) Cu; (very weak) Ga, V, Sn, Y, Yb, Ag. The Sc content is about 3%. X-ray study showed the structure to be of the beryl type with space group probably $D_{6h}^{2-}P6/mcc$ (possibly $C_{6v}^{2-}P6cc$) with $a=9.50$, $c=9.18$ Å.

DISCUSSION: Bazzite, which has never been analyzed chemically, was originally described as a scandium silicate, the beryllium content having been missed. The close correspondence of the unit cell, hardness, specific gravity, and composition makes it seem likely that bazzite is a scandian beryl. The indices of refraction and birefringence are higher than those reported for any beryl (due to Fe and Sc?), which suggests that cesium may be present in appreciable amount. Dr. W. T. Schaller suggests the possibility that some crystals from various localities identified by sight as blue tourmaline could be bazzite, although the absorption schemes are reversed.

M. F.

DISCREDITED MINERALS

Wenzelite, Baldaufite (= Hureaulite)

H. STRUNZ, Identität von Wenzelit und Baldaufit mit Huréaulith. *Neues Jahrb. Mineral., Monatsh.* 1954, 166-177.

Chemical analyses, optical data, and x-ray powder data on samples from the type locality, Hagendoff, Bavaria, show that the original analyses (Müllbauer, 1925) were incorrect and that both minerals are hureaulite.

M. F.